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Experimental efforts were concentrated upon optimizing the leaching process. Preferred leaching conditions were defined. With two-stage leaching at 50 C in concentrated ammonium carbonate, the copper-plus-nickel content can be reduced to a level of less than 1 percent from an original content on the order of 10 percent. By roasting the depleted sludge with soda ash, at least 80 percent of the chromium can by recovered in water-soluble form. Controlled-potential electrodeposition was shown to be capable of separately winning copper and nickel values from the pregnant ammoniacal leaching liquor.

A process flow sheet is presented, and process economics are reviewed. The economic evaluation indicates that it is probable that these operations will be a net expense. The process studied would be an alternative only if costs for disposal of sludge rose to the highest part of the current range.

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AMMONIUM-CARBONATE LEACHING OF METAL VALUES FROM WATER-TREATMENT SLUDGES

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory--Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

As a part of these kinds of activities, this study was undertaken specifically to explore and to develop processes based on the ammoniacal leaching of metal-bearing sludges that are produced during wastewater treatment operations in the metal-finishing (and related) industries. The major objective was to eliminate or to reduce sufficiently the heavy-metal content of the sludge so that it would no longer constitute a potential ecological hazard. Removal of copper and nickel from the sludge constitutes the first step in the recovery and recycle of these important metal commodities. The results reported herein can be utilized by those who need to remove copper and nickel from mixed-metal-bearing sludges for the purposes of detoxification and resource recovery.

For further information on this subject, contact the Industrial Pollution Control Division, Metals and Inorganic Chemicals Branch.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

Many of the potential hazards accompanying the unrestricted disposal of wastes from biological and industrial processes have been recognized for many years. Only in recent years, however, have the complexity and intensity of the problems involved in waste management and disposal reached the point where the quality of the air-land-water environment is critically impaired in many geographical areas. As efforts to curb pollution have been intensified, legal standards have been made more strict.

Industrial wastes have contributed heavily to the degradation of the quality of man's environment, and many industries have invested considerable effort to abate pollution. The waterborne wastes produced in metal-finishing operations, particularly, are such that complex and costly methods have been needed to prevent the contamination of water supplies with the toxic compounds used in these operations.

The specific steps involved in the treatment of metal-finishing wastes vary considerably from installation to installation. However, the general treatment consists of (1) separation of grease and oil, (2) reduction of chromates, (3) destruction of cyanides by oxidation, (4) neutralization of the waste streams, and (5) separation and disposal of the sludges. The metals initially present in the wastewaters are precipitated as hydroxides and appear in the sludges.

One of the most troublesome and costly aspects of the treatment of metal-finishing wastes is the final disposal of the metal-bearing sludges that appear in Step (5). Increasing congestion of urban areas in which many of the larger plating facilities are located, together with the accompanying increases in the cost of land, adds to the problems involved in ultimate disposal.

These sludges may contain large quantities of relatively valuable metals--nickel, chromium, cadmium, titanium, etc.--which often are in short supply. The values of the nickel and chromium lost in plating waste in the United States has been estimated at 25 to 30 million dollars per year (1975). Sludges selected from various steps in the waste-treatment procedure may contain 10 to 15 percent of nickel, chromium, etc., on a dry basis--concentrations greater than those found in most ores containing these metals. The economic feasibility of recovery would be largely dependent on the size of the plating facility, the cost of the primary raw materials used in the plating operations, and the cost of alternative methods of sludge disposal, e.g., lagoons, landfills, etc.

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Because of the importance of eliminating potential waste-control problems, while concurrently recovering valuable materials, an investigation of the possible recovery of metals from sludges produced during the treatment of metal-finishing wastes was undertaken. Additional considerations in this undertaking were that this is a general problem in the metal-finishing industry and a large segment of the industry would realize benefits from a successful study.

ABSTRACT

This project was undertaken to explore and develop processes based on ammoniacal leaching to recover metal values from metal-finishing wastewater treatment sludges. The objective was to eliminate or to reduce sufficiently the heavy metal content of the sludge so that it would no longer constitute a potential ecological hazard, thus greatly reducing the cost of sludge disposal. Metallic copper and nickel were to be recovered by electrodeposition from the filtered ammoniacal leachant and chromium (as chromate compound) from the depleted sludge by a carbonate roast followed by water leaching. The market value of these recovered materials would at least partially offset the costs of the stripping and metal recovery, and at best would net a profit.

Early leaching experiments revealed greater difficulty than expected in obtaining satisfactory depletion of the sludge. Consequently, experimental efforts were concentrated upon optimizing the leaching process. Preferred leaching conditions were defined. With two-stage leaching at 50 C in concentrated ammonium carbonate, the copper-plus-nickel content can be reduced to a level of less than 1 percent from an original content on the order of 10 percent. By roasting the depleted sludge with soda ash, at least 80 percent of the chromium can be recovered in water-soluble form. Controlled-potential electrodeposition was shown to be capable of separately winning copper and nickel values from the pregnant ammoniacal leaching liquor.

A process flow sheet is presented, and process economics are reviewed. The economic evaluation indicates that it is probable that these operations will be a net expense. This net expense falls within the very wide range of costs reported for sludge disposal. The process studied would be an alternative only if costs for disposal of sludge rose to the highest part of the current range.

This report was submitted in fulfillment of Grant No. R803787-01 by Battelle's Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 1, 1975, through October 31, 1976, and work was completed as of July 31, 1976.

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The program was guided and monitored by Mr. D. J. Wilson of the Industrial Pollution Control Division of the Industrial Environmental Research Laboratory and Mr. Charles J. Rogers of the Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, both at Cincinnati. The support of the program was shared by those respective organizational units.

SECTION 1

INTRODUCTION

The treatment of wastewaters from 15 to 20,000 metal-finishing facilities in the U.S. generates large amounts of sludge that require disposal. The sludges are neutralized prior to disposal and contain concentrations of heavy metals according to (1) the metals, alloys, and finishing operations conducted in the plants and (2) the specifics of wastewater treatment or management practiced by the plants. Some of these heavy metals are ecologically objectionable. Further, they represent wasted resources, which, if recovered, would have substantial market value.

Both the ecological penalties and the financial incentive for recovery of any heavy metals contained in such sludges depend upon the concentration of the individual metals contained. Sludges that may contain percentages of metals such as copper, nickel, cadmium, or chromium would probably benefit by further treatment to reduce the level of these ecologically objectionable, or even hazardous, components to a level of less than 1 percent. If this could be achieved in a manner that would allow reclamation of the metals in marketable forms, the return from sale or reuse of recovered material might be used to offset the cost of the required additional disposal procedures or safeguards.

Chromium, copper, and nickel are three heavy metals common at levels up to 10 or 15 percent (dry) in many sludges derived from metal-finishing operations. Two of these, copper and nickel, are recoverable from low-grade resources by ammoniacal leaching.*

Laboratory studies have shown that the metal values extracted from metal-finishing sludges by ammoniacal leaching can be recovered by electrolysis.** Furthermore, because chromium, which is most often associated with copper and/or nickel in metal-finishing sludges, is not complexed during ammoniacal leaching, pregnant ammoniacal leach liquors should be relatively

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* Hewedi, M. A., and L. R. Engle. The NH_3-CO_2-H_2O System at Atmospheric Pressure in Nonferrous Extractive Metallurgy. International Symposium on Hydrometallurgy. AIME, Chicago, Illinois, 1973.

** Tripler, A. B., R. H. Cherry, Jr., and G. R. Smithson, Jr. Reclamation of Metal Values from Metal-Finishing Waste Treatment Sludges. Report EPA-670/2-75-018. Battelle's Columbus Laboratories, April, 1975. 89 pp.

free of chromium interference during electrolysis for copper or nickel. This would not be the case, for example, in acid leaching, which solubilizes most metal values (including chromium). Preference for ammoniacal leaching is based in part on the knowledge that most sludges tend to be basic in character (neutralized with lime--metals are probably contained in hydroxide form) and acid leaching would require considerable acid waste in counteracting the contained calcium before leaching would proceed at lower pH levels. Ammonium chemicals are relatively expensive, but the ammonia values would not be consumed chemically and would be recycled in a leaching scheme designed around their use.

The original objectives of the present program were to (1) demonstrate that rapid and complete leaching of copper and nickel values could be accomplished from a typical metal-finishing sludge, (2) establish procedures and demonstrate the direct recovery of metallic copper and nickel values from the pregnant leach liquor by electrolysis, (3) investigate the applicability of a carbonate-roast/water-leach treatment for recovery of chromium after ammonium carbonate leaching of copper and nickel, (4) combine operations in an integrated process amenable to portable demonstration, and (5) estimate the process costs. Underlying these objectives was the assumption that the processing would reduce the copper, nickel, and chromium levels of the sludge to a point where the residuals of these metals would not be environmentally objectionable.

The results of early experiments with leaching indicated considerably greater difficulties in obtaining satisfactorily complete leaching of the contained copper and nickel values than had been anticipated. Without at least 90 percent reduction in the original copper and nickel contents of the sludge, achievement of Objectives (2)-(5) was deemed academic. Consequently, when this problem was not resolved in early experiments, a revised scope was requested and approved by EPA. With this revision, the primary objective became the demonstration of at least 90 percent removal of the contained copper and nickel values from the sludge by leaching with ammonium carbonate. It was towards this objective that experiments in the later stages of this program were directed.

SECTION V

CONCLUSIONS

Experimental studies in this program were concentrated on defining an ammoniacal leaching practice that would maximize the return of copper and nickel values from metal-finishing sludges to the leach solution, while at the same time minimizing the dissolution of chromium values. In relation to this primary objective, the following conclusions are presented, with the general assumption that the specific sludge examined is representative of copper-, nickel-, and chromium-bearing sludges.

(1) The raw sludge is best leached without resorting to drying or grinding before leaching. Drying and grinding of the sludge before leaching undesirably increases the fraction of contained chromium that dissolves during leaching with ammonium carbonate.

(2) The preferred leachant is ammonium carbonate. This salt is conveniently added to mixtures of water and sludge. The strength of the aqueous phase is maintained at a level of approximately 10 percent contained NH_3 for best results.

(3) Leaching extractions are most rapid where leaching is conducted at a temperature of 50°C.

(4) The return of nickel to the aqueous phase is inhibited (probably by the pH of the leach solution) when the aqueous phase is rich in copper, and vice versa. For this reason, leaching of sludges containing both copper and nickel is best conducted in two stages, each comprising 2 to 3 hours of leaching time. Interstage processing involves the separation of the liquid and solid phases, so that the subordinate metal during the first stage of leaching is allowed to dominate reactions in the second stage.

(5) No advantages were found to support the use of either ammonium sulfate leaching or ammonium hydroxide fortification of the ammonium carbonate leaching solution.

(6) Ammonium carbonate leaching is a practical method for reducing the copper and nickel contents of sludges to

levels of less than 1 percent, probably to levels on the order of 1/2 percent or slightly lower. (Original sludge samples contained 5-9 percent copper and 0.8-1.2 percent nickel by weight on a dry basis.) However, some residual copper and nickel values in sludges are apparently refractory against aqueous complexing in ammoniacal solutions.

Based upon the results of these limited studies, it is further concluded that chromium values in the sludge can be largely removed by roasting with sodium carbonate, followed by water leaching of the fused mass to return soluble chromates or dichromates for recovery from the aqueous leach solution. Studies were not sufficiently extensive to define precisely the recovery limits; an 80 percent reduction in the chromium content of the sludge was demonstrated. For sludges containing more than 10 percent chromium, this recovery level constitutes a significant resource of chromium for recycling.

The recovery of the metals copper and nickel from pregnant aqueous liquors was studied only briefly. The technical feasibility of recovering metals from ammoniacal solutions, either by electrowinning or by cementation with zinc, was indicated.

Treatment of the raw, dried sludge used in this experimental program by ammonium carbonate leaching to remove copper and nickel appears to have reduced the susceptibility of the treated residue to further attack, both by simulated acidic rainwater and by organic acids, such as acetic acid. The evidence in support of this conclusion is derived from a single set of leaching experiments. The acceptability in terms of reduction of hazard or of insult to the environment cannot be judged until suitable regulations applicable to hazardous materials containing heavy metals are promulgated.

The economics of such a metals recovery operation were examined in terms of a projected plant assumed to process 100 tons per day of raw (i.e., 20 percent solids) sludge and recover copper, nickel, and anhydrous chromic acid as principal products. The capital cost of such a plant was estimated to be in the range of 3-5 million dollars and the daily operating costs, after credits were allowed for sale of the copper, nickel, and CrO_3, were estimated to amount to a net outlay. This cost was compared to the results of a survey of sludge treatment and disposal costs which reported costs of from $6/ton to $60/ton for treatment and disposal, depending on the type or method of disposal, the nature of the waste, geographical location, and general variations among disposal contractors and local regulations. It was concluded that the cost associated with the process, while not representing a profit-making situation, might become an alternative of choice should either the prices of metals increase or the disposal of the raw sludge become the subject of stringent regulation because of the metals content.

SECTION 9

RECOMMENDATIONS

The major finding of this study is that the treatments investigated can be used to lower the copper, nickel, and chromium in metal-finishing sludges from a level on the order of 10 to 20 percent to a residual level on the order of 1 percent. This reduction would undoubtedly significantly decrease the risk of groundwater contamination associated with sludge storage.

Estimates of the costs of processing indicate that, under current conditions, the net cost of processing in a projected plant falls within the very wide range of current disposal costs. This wide range of disposal costs prevents any firm recommendation regarding economic feasibility of the process studied. Future events that could change this point of view would be (1) disproportionate increases in the prices of chromium, nickel, and/or copper, or shortages of these metals, and (2) increased costs associated with the disposal of sludges, which would be substantially decreased if metal values were removed using the process studied.

In view of these factors, it is recommended that the results of this study be periodically evaluated in terms of regulations concerning the designation and disposal of hazardous wastes and further development studies be keyed to the needs indicated by these regulations.

SECTION 4

MATERIALS AND EQUIPMENT

The experimental work described in this report was conducted on samples of sludge extracted from the sludge storage lagoon of the Ametek U.S. Gauge plant at Sellersville, Pennsylvania. Brass, steel, and copper-nickel alloys are the principal materials processed by Ametek. Operations that contribute metal values to the sludge include pickling, bright dipping, deburring, and electroplating (chromium, cadmium, tin, lead, nickel, and cyanide zinc).

The sludge is largely generated in the wastewater treatment processes, which include collection, neutralization (with lime), cyanide destruction, and chrome reduction. Treated wastes are settled in one of two wet lagoons, from which the sludge is removed periodically to the storage lagoon.

An initial 18 kg sample of sludge was collected in July, 1975, and transported to Battelle for initial experiments. Solids content was determined to be about 20 percent. Analyses showed the dried and blended solids to contain 17.2 Cr, 8.7 Cu, and 1.1 Ni (percents by weight). A second sample of 213 kg was taken and shipped to Battelle in September, 1975. This was dried at nominally 110 C, resulting in a solids weight of 46 kg. Analytical results for elements of particular interest contained in the blended dry sludge were (percents by weight) 12.8 Cr, 5.8 Cu, and 0.91 Ni, with standard deviations (at least six observations) of 0.82, 0.24, and 0.07, respectively. Supplementary analysis of the dried sludge indicated (percent by weight) 6.7 Si, 5.7 Ca, 4.1 Al, 2.0 Na, 1.6 Fe, 0.9 Mg, and 2.5 C.

The dried sludge was further characterized to determine its water solubility. Samples were stirred in demineralized, double-distilled water for 3 hours, followed by filtration and analyses. It was determined that 10 to 11 percent of the dried sludge was water soluble or was volatilized during drying of the filter cake at 105 C. Analyses of the filtrate indicated a total solids content (evaporated at 103 C) of about 9.7 percent, with solute analyses as follows:

Solute Specie	Content, gm/100 gm sludge
Sulfate	6.3
Sodium	2.1
Calcium	0.65
Chloride	0.23
Magnesium	0.20
Organic carbon	0.05
Silicon	0.01

Solute Specie	Content, gm/100 gm sludge
Inorganic carbon	0.006
Chromium	0.007
Potassium	0.007
Nitrate-nitrite nitrogen	0.003
Nickel	0.001
Cu, Mn, P, Fe, Zn	<0.001 ea
Total identified	9.6

Thus, the heavy metals contained in the sludge are virtually insoluble in water.

A special series of leaching experiments was conducted on cupric, nickelous, and chromic oxides and hydroxides. These were purchased as fine powders, except for chromic hydroxide, which was available only as a relatively coarse powder. Sources and purities are indicated in Table 1. These materials were used in the condition in which they were received.

Chemicals used in all leaching experiments were usually reagent grade. Lot assay data were available for ammonium carbonate, ammonium hydroxide, and ammonium sulfate, which were the principal leachate components explored. Leaching and wash media were prepared using demineralized, double-distilled water. Reagents used in analyses of filtrates, sludge, and filter cakes for copper, nickel, and chromium were prepared and standardized at Battelle using reagent grade chemicals. Periodic analytical checks were made using atomic absorption equipment by TraBet, a local commercial testing laboratory.

No specific equipment was required for the performance of this program. Leaching and limited electrolytic studies were conducted in conventional laboratory glassware and employed available equipment (stirrers, rectifiers, ovens, pressure filter, etc.).

TABLE 1. OXIDE AND HYDROXIDE DESCRIPTIONS

	Supplier	Grade	Assay Weight Percent	Basis
CuO	Mallinckrodt	Reagent	79.5 Cu	≈ 0.5 percent impurities
$Cu(OH)_2$	Atomergic Chemicals	"99%"	64.4 Cu	99 percent $Cu(OH)_2$
NiO	Baker	Reagent	77.9 Ni	99.1 percent NiO
$Ni(OH)_2$	Alfa-Ventron	Reagent	61.6 Ni	"Typical assay"
CrO_3	Baker	C.P.	68.4 Cr	Assumption
$Cr(OH_3)$	Alfa-Ventron	Technical	38.5 Cr	76.2 percent $Cr(OH)_3$

SECTION 5

EXPERIMENTAL PROCEDURES

SLUDGE PREPARATION

To facilitate quantitative evaluation of results, both sludge samples were dried at 110 C to remove free water. The dried sludge samples were then crushed, ball-milled (dry) and tumble-blended (as two lots) in a plastic barrel. Analytical details of these lots are given in Table 2.

For later experiments, two nominal 1-kg samples of the Lot 2 dried sludge were further wet ball-milled in a ceramic mill. Each sample was ground with 2-1/2 liters of water. The resulting slurries appeared to be quite stable suspensions and were determined (by redrying at 110 C) to contain 28.5-29 percent solids as expected. Analyses on these slurry samples were compatible with those of the Lot 2 dried sludge from which they were prepared, except for nickel. For the first of the slurry samples (Sample No. 1), nickel was analyzed to be 1.3 weight percent [with a standard deviation of 0.009 (four analyses)], which was somewhat greater than the expected value for the Lot 2 dried sludge. Nickel in slurry Sample No. 2 was analyzed to be 0.96 percent, in accord with the Lot 2 value.

LEACHING PROCEDURES

Leaching was conducted in 2 or 3-liter glass beakers. For leaching of the raw sludge (Lot 1 with 19.5 percent solids was used for these early experiments), 500-gram samples of sludge (97.5 grams of solids) were weighed immediately after homogenizing with a paint stirrer. For leaches of dried sludge, 100-gram samples were weighed when withdrawn from the plastic storage barrel in which the dried sludge had been tumble-blended. Leaches conducted on the wet-ball-milled sludge slurries used 350-gram samples containing 102.5 grams of solids. These samples were weighed immediately after stirring of the slurry batch for homogenization. The sample to be leached was placed in a beaker, which usually contained a predetermined amount of water. The leachate and its method of addition varied for the numerous experiments that were conducted. In all cases, the weight ratio of solids to be leached to leaching solution was within the range of 1:9 to 1:14. Nominally, leaches comprised 100 grams of solids and one liter of leachant. Leachant make-up and strengths were as follows:

(1) Premixed $(NH_4)_2CO_3$ plus NH_4OH to result in a leachant strength of 6.5 contained NH_3:CO_2, in percent by weight.

TABLE 2. RESULTS OF SLUDGE ANALYSIS*

	Lot 1	Lot 2
Percent Solids		
n	3	4
$\bar{x}$	19.5	21.75
s	0.03	1.26
Copper, Weight Percent, Dry Basis		
n	3	6
$\bar{x}$	8.7	6.0
s	0.2	0.236
95 percent confidence range	7.84 - 9.56	5.19 - 6.41
Nickel, Weight Percent, Dry Basis		
n	3	9
$\bar{x}$	1.09	0.91
s	0.02	0.07
95 percent confidence range	1.00 - 1.18	0.75 - 1.07
Chromium, Weight Percent, Dry Basis		
n	3	6
$\bar{x}$	17.2	12.8
s	0.27	0.82
95 percent confidence range	16.0 - 18.3	10.7 - 14.9

* In this table: n = number of observations; $\bar{x}$ = mean value; and s = standard deviation.

(2) Same as above, but at a strength of 11:9.

(3) Same as above, but at a strength of 25:14. (This was nearly saturated.)

(4) NH_4OH at two strengths:

  (a) Concentrated (29 weight percent NH_3)

  (b) Dilute (6 weight percent NH_3).

(5) $(NH_4)_2CO_3$ at three strengths:

  (a) Dilute (5 weight percent NH_3)

  (b) Saturated at room temperature

  (c) Supersaturated at room temperature (9 weight percent NH_3). This was used in two forms: premixed and as a direct addition to a stirred sludge-water mixture.

(6) Premixed $(NH_4)_2SO_4$ (200 g) and NH_4OH (40 ml of 29 percent NH_3) to a leachant volume of 1 liter. Strength was 5 weight percent NH_3.

For leaching experiments conducted at elevated temperature which used a direct addition of $(NH_4)_2CO_3$ as the leachant, the water-sludge slurry was usually heated to about 5 degrees warmer than the planned leaching temperature to accommodate the loss of temperature upon addition of the $(NH_4)_2CO_3$, which dissolves endothermically. In all cases, the water-sludge mixture was thoroughly stirred with a propeller to effect a vortex that extended nearly to the bottom of the beaker. This stirring commenced prior to the addition of the leachant and continued throughout the experiment. Stirring was interrupted only briefly to allow the taking of grab samples for intermediate analyses during some of the experiments. Leaching time was measured from the time of leachant addition to the time the stirrer was shut off. Upon conclusion of leaching, the mixtures were pressure filtered. Beaker contents were chased with distilled water into the filtration vessel. The usual time lapse between the end of leaching and the beginning of pressure filtering was not greater than 10 minutes. Leaching times ranged from 2 to 64 hours.

For staged leaching experiments, most of the wet filter cake was transferred to a beaker containing 200 ml of water, and the filter paper was rinsed in a second beaker. Then the contents of the two beakers were combined for the next stage of leaching.

During leaching, beakers were covered with a hinged plexiglass lid to prevent splash losses. Holes for the stirrer shaft and a thermometer or thermocouple (used with a recorder for extended leaches) were provided.

For leaching experiments where grab samples were taken, the stirrer was stopped, half of the lid raised, and the sample (nominally 80 ml) was dipped from the top of the mixture, the lid closed, and the stirrer started again. This procedure normally took about 10 seconds. The grab samples were then gravity filtered, and filtrates were analyzed for copper, nickel, and chromium. In a few cases, the residues were dried, weighed, and analyzed as well.

In addition to chemical analyses of filtrates and selected head stock and filter cakes, data that were regularly obtained were filtrate (including wash water) volume and weight and wet and dry filter-cake weights (with proper tares for vessels and papers). Final filtrate volume measurements were accurate to roughly 1 percent, and weights were accurate to within about 1/2 percent, with some uncertainty attached to the filter paper tare value.

Intermediate data relating to analyses and calculations based on grab samples were less accurate because of the crudeness in estimating volume of the leaching mixture. The leaching beakers were graduated in 100 ml increments. Graduation marks were probably accurate to about ± 10 ml. Estimates of mixture volume (made while the stirrer was off) were to the nearest 10 ml and were probably accurate to only ± 10 ml. Frequently, a layer of 1 to 5 cm of foam, not counted in the mixture volume, was present. No allowance was made for the uncertain volume of the suspended solids, which was probably on the order of 20 ml. Inaccuracies due to foaming and solids would tend to offset each other. Because of these uncertainties, intermediate data are probably only accurate to about ± 30 ml, or roughly 3 percent of the volume of the mixture. These inaccuracies, however, did not influence the conclusions drawn on the basis of the data generated. Calculations describing the cumulative leaching action in experiments where grab samples were taken included progressive consideration of metal values removed in the grab samples, both in solution and as suspended solids (the latter prorated except where filter residues were weighed and analyzed).

ANALYTICAL PROCEDURES

The procedures used in the determination of concentrations of copper, nickel, and chromium in samples of sludges, filtrates, and filter cakes are given in Tables 3, 4, and 5. The results obtained with these methods were checked periodically by submitting duplicate samples for atomic absorption analyses at a commercial laboratory. Good checks were obtained.

All analyses were conducted at least in duplicate. Thus, each reported analysis was the average of two or three individual results and had a sample standard deviation associated with it. During this program, evaluations of these standard deviations were made wherein the standard deviations were assumed to be normally distributed and were pooled. At least ten analyses of each type were considered. The pooled values, with their associated degrees of freedom, were used to estimate the variability expected at the 90 percent level of significance. For copper and nickel, analyses of solids

TABLE 3. ANALYTICAL PROCEDURES FOR COPPER DETERMINATIONS

For sludge, a filter residue--0.2-gram samples, weighed to nearest 0.1 mg.

For leach filtrate--2 ml (pipette) add 25 ml H_2O--boil gently for 5 minutes with chips.

1. Add 5 ml concentrated HCl and 2 ml concentrated HNO_3 in a 250 ml Erlenmeyer flask.
2. Digest slowly and evaporate to dryness (brown color).
3. Add 3 ml concentrated HCl and evaporate to dryness again to drive off the last of the nitrates.
4. Cool and add 80 ml of H_2O.
5. Make faintly ammoniacal by adding 1:1 NH_4OH from a burret.
6. Add 10 ml concentrated acetic acid and boil for 1 minute (use boiling chips).
7. Cool; then 3 minutes before ready to titrate, add one porcelain spoonful of sodium fluoride and one spoonful of potassium iodide. Let stand for 1 minute.
8. Add 3 ml starch indicator just before beginning titration; titrate with 0.02 N sodium thiosulphate to pale blue end point.

Percent copper in residue or sludge:

$$= \frac{6.354 \times \text{ml of } Na_2S_2O_3 \times \text{normality of } Na_2S_2O_3}{\text{weight of sample, g}}$$

$$= \frac{63.54 \times \text{ml } Na_2S_2O_3 \times \text{normality of } Na_2S_2O_3}{\text{volume of sample, ml}}$$

TABLE 4. ANALYTICAL PROCEDURES FOR NICKEL DETERMINATIONS

For sludge in filter residue - 0.5-gram samples, weighed to nearest 0.1 mg.

For leach filtrate - 20 ml (pipette) add 25 ml H_2O - boil gently for 5 minutes with chips.

1. Put samples in 400 ml beaker and add 30 ml 1:1 H_2SO_4 and 4 ml concentrated H_3PO_4.
2. Fume for 10 minutes at high heat.
3. Cool and add 3 ml concentrated HNO_3.
4. Boil to drive off reddish brown fumes until white fumes of SO_3 start to evolve.
5. Cool and add 100 ml H_2O and stir (heat if necessary) to dissolve salts.
6. Filter through a Wattman 541 paper. Wash 5 times alternately with 5% HCl and hot water. Discard paper and precipitate.
7. To the filtrate and washings, add 25 ml citrate-sulfate solution.*
8. Warm on hot plate to about 50 C and add 25 ml dimethyl glyoxime** solution.
9. Add concentrated NH_4OH until faintly ammoniacal (blow and smell) to precipitate nickel.
10. Digest 30 minutes at 60 C, then for 3 hours or longer at room temperature.
11. Filter through weighed sintered-glass crucible. Wash at least 5 times with cold water.
12. To filtrate, add 5 ml dimethyl glyoxime solution to certify complete precipitation.
13. Dry crucible and precipitate at 130-150 C for 1 hour.
14. Cool in a desiccator and weigh.

* 200 g citric acid monohydrate in 1 liter dilute (1:9) H_2SO_4.

** 10 g dimethyl glyoxime in 1 liter absolute alcohol.

TABLE 4. (Continued)

Percent nickel in residue or sludge

$$= \frac{20.32 \times \text{grams dimethyl-glyoxime nickel precipitate}}{\text{weight of sample, g}}$$

g/l nickel in solution (filtrate)

$$= \frac{203.2 \times \text{grams dimethyl-glyoxime precipitate}}{\text{volume of sample, ml}}$$

TABLE 5. ANALYTICAL PROCEDURES FOR CHROMIUM DETERMINATIONS

For sludge or filter residue - 0.2-gram samples, weighed to nearest 0.1 mg

For leach filtrate - 20 ml (pipette) add 25 ml H_2O - boil gently for 5 minutes with chips.

1. Put samples in a 400 ml beaker and add 20 ml H_2SO_4 (1:1), 3 ml concentrated H_3PO_4.
2. Fume for 10 minutes and cool.
3. Add 3 ml concentrated HNO_3 and boil to drive off reddish brown fumes of nitrogen.
4. Cool and add 100 ml of H_2O.
5. Add 5 ml of 2% $AgNO_3$ and 20 ml of 10% ammonium persulfate and boil for 10 minutes.
6. Cool and with a pipette add 50 ml of 0.1 N ferrous ammonium sulfate solution.
7. Titrate excess of the ferrous ammonium sulfate with 0.1 N $KMnO_4$ until a change in color persists for 2 minutes.

A = ml $KMnO_4$ required to react with total amount of ferrous ammonium sulfate added.

B = ml $KMnO_4$ used in back titration.

$$\text{Percent chromium in residue} = \frac{1.733 \times \text{normality of } KMnO_4 \times (A-B)}{\text{weight of sample, g}}$$

$$\text{g/l chromium in solution (Filtrate)} = \frac{17.33 \times \text{normality of } KMnO_4 \times (A-B)}{\text{volume of sample, ml}}$$

exhibited about twice the variability as was associated with analyses of filtrates, as indicated below.

Element	Expected (90 percent significance) ± Variability, percent of reported value	
	Solids	Solutions
Cu	11	5
Ni	11	6
Cr	5	6

Reasons for these variations were not determined but are believed to be related to sampling or analysis techniques. It is important to be aware of these variabilities, or limitations on accuracy, in considering the experimental results and in arriving at conclusions based on them.

CHROMIUM OXIDATION

Metal-finishing sludges are the product of waste-treatment practices that include operations designed to reduce chromium to the chromic state (insoluble in water) from the chromate or dichromate state (water soluble). Chromic chromium is reportedly unaffected by leaching in ammonium salts, and chromium thus largely remains with the solid residue after leaching, effecting a desirable segregation of metal values. Because of the high level of chromium in many sludges, its recovery would be economically desirable.

A series of roasts of high-chromium leaching residues in the presence of soda ash (Na_2CO_3) was conducted to briefly evaluate the feasibility of chromium recovery via reoxidizing it to the +6 valence state and leaching the product in water. In these studies, the residue from a 20-hour leach of raw sludge from Lot 1 (17.2 percent Cr) was used. Before roasting, the residue was determined by analysis to have a chromium concentration of 22.2 weight percent on a dry basis.

The roast/leach procedure for chromium conversion and solution was as follows:

(1) Two grams of dried residue was blended with 3-1/2 grams of Na_2CO_3 in a crucible. (This represents about a 50 percent excess of the stoichiometric requirement for Na_2CrO_4 formation from Cr_2O_3.)

(2) The crucible and its contents were brought to a red heat, and the fused mass was maintained at temperature for 1 hour.

(3) After cooling, the fused mass was broken up and dissolved in distilled water.

(4) The mixture was filtered through a slow paper and the residue washed until the filtrate was colorless.

(5) Filtrate and wash were combined and diluted to 500 ml. Chromium analyses were made on this diluted volume.

This experiment was conducted in duplicate.

RECOVERY OF METAL VALUES

One can visualize a general type of process for the leaching of metal values from a sludge in which leach liquor is circulated continuously between the leach vessel and a process subsystem for the removal of one or more of the metals dissolved in the liquor. The leach liquor is returned to the leach vessel after passing through this subsystem. After the original sludge has been depleted of its content of heavy metals, the treated, detoxified sludge is discharged. The process sequence is then repeated.

Candidate subprocesses for the removal of metals from the leach liquor include, but are not necessarily limited to, the following:

- Electrolysis to win metals from ammonium carbonate leach liquors
- Cementation of metals from ammonium leach liquors
- Selective precipitation by the addition of appropriate reagents to the leach liquor.

The first two of these candidate subprocesses offer the advantage that metal values are produced as such; they are described under Metal Winning Experiments.

The last of these candidate subprocesses offers some possible advantages, such as a quick, simple means of removing from the leach liquor dissolved metals (e.g., copper and nickel), which display apparent antagonistic effects in terms of mutual solubility in the leach liquor.

Electrolysis

Electrowinning experiments for the recovery of copper and nickel were conducted before actual leaching filtrates were available. Synthetic sludges were prepared by precipitating salts of copper, nickel, chromium, zinc, and iron as hydroxides in aqueous solution, and precipitation of aluminum as the phosphate. The precipitates were then leached in 1M $(NH_4)_2CO_3$ to simulate the complexing action expected during leaching and filtered. If all the precipitates had returned to solution upon treatment with ammonium carbonate, concentrations, in g/l, would have been 4 Cu, 0.4 Ni, 10 Cr, 0.5 Zn, 2 Fe, and 5 Al. The pH of the filtrates (six solutions with varying combinations of metals were explored) ranged from 8.75 to 9.40, and conductivities ranged from 84,000 to 93,000 μmho-cm.

Electrolysis experiments were conducted on the above filtrates in a three-compartment cell, with catholyte and anolytes separated by a medium-pore glass frit. Active electrodes were of platinum. A calomel electrode was contained in the third cell, and a capillary bridge referenced this electrode to the catholyte. Experiments were conducted at controlled potentials designed to deposit copper at the higher potential and nickel (plus zinc) at a somewhat lower potential.

Observations in these preliminary studies were largely qualitative and concerned the color and nature of deposits as the electrolytes were depleted. The dependence of current density upon solute concentration for the depositing species was observed.

Cementation Studies

Samples of leaching filtrates were subjected to cementation. In these beaker studies, metallic zinc or iron was added to the filtrate with the intent of replacing the contained copper and nickel in solution by a more electronegative metal. The resulting solutions were filtered and analyzed for copper and nickel. Additional details are given in the Results Section.

Precipitation with Sodium Aluminate

Ammonium carbonate leach liquor containing copper, nickel, and chromium was treated with an aqueous solution of sodium aluminate. The sodium aluminate solution was prepared by adding aluminum powder to a strong sodium hydroxide solution until all evidence of hydrogen evolution ceased. The sodium hydroxide solution was prepared by adding approximately 5 grams of reagent-grade solid sodium hydroxide to 100 ml of demineralized water. The results are presented in Section 6.

TESTS FOR ACID LEACHABILITY OF SLUDGE AFTER TREATMENT TO REMOVE COPPER AND NICKEL

It was judged necessary to obtain an experimental indication of the effectiveness of the ammonium carbonate leaching of copper and nickel in producing a treated sludge that would be less subject to attack by the environment and one which therefore would be more acceptable in terms of insult to the environment. Samples of dried, treated residue from Experiments 35B and 36B (after two-stage ammonium carbonate leaching of the original sludge were exposed for 24 hours to

(1) Simulated (sulfuric) acid rainwater (pH 4)

(2) Simulated acidic environment in a landfill (1 percent by volume glacial acetic acid in water).

For purposes of comparison, two samples of untreated dried sludge (which had not been leached with ammonium carbonate) were exposed to these same acid environments. The results of these exposures are described in Section 6.

SECTION 6

RESULTS AND DISCUSSION

LEACHING STUDIES

Leaching studies were conducted to evaluate the influence of (1) pretreatment of sludge, (2) leachant type and strength, (3) leaching temperature, (4) leaching time, (5) aeration and CO_2 sparging, (6) loading of the leach liquor, (7) oxide vs. hydroxide forms of contained metals, and (8) staged leaching. Detailed descriptions of the individual experiments are tabulated in Appendix A, Table A-1.

The principal criteria for evaluation were chemical analyses of filtrates to determine the degree of extraction from the sludge of copper, nickel, and chromium during the leaching experiments. Analytical data obtained on filtrates and residual solids are listed in Appendix A, Table A-2. Quantitative data calculated from measurements and analyses are presented in Table A-3, and the results of recovery calculations and accountabilities are reported in Table A-4.

As discussed previously, it was the objective of these studies to maximize the amounts of copper and nickel extracted (dissolved in the pregnant leach liquor), while minimizing the extraction of chromium. Judgmentally, it was assumed that at least 90 percent extraction of both copper and nickel would be required for returns to be considered satisfactory.

Sludge Pretreatment Effects

Four forms of the Ametek sludge were examined in the various leaching experiments. These were (1) the raw sludge, which contained about 20 percent solids; (2) sludge that had been dried at 110 C, then comminuted and blended; (3) dried sludge that had been ball-milled with water to create a slurry suspension; and (4) dried sludge that had been washed with water to remove about 10 percent of its weight as water-soluble material, followed by filtering, redrying, and grinding.

The single experiment with sludge which had been water-washed to remove water-soluble constituents suggested that water-washing was detrimental to both nickel and copper recoveries. The percentages of the copper, nickel, and chromium which were dissolved during leaching (relative to the amounts which were in the sludge before leaching), expressed as percent extracted, were as follows:

Copper:	34 percent
Nickel:	11 percent
Chromium:	4 percent

Other sludge pretreatments evaluated in leaches at room temperature showed no significant effects on extractions, but some weak trends may be present, particularly relative to an undesirable increase in chromium solubility resulting from reslurrying.

	Raw Sludge	Dried Sludge	Reslurried Dried Sludge
Experiment numbers[a]	1,2,3	8,9,11,15,16,17,18	29
Copper			
Average, percent	57	53	56
Standard deviation	4.2	6.3	--
Nickel			
Average, percent	19	30	19
Standard deviation	7.1	10.6	--
Chromium			
Average, percent	2	7	15
Standard deviation	2.1	4.7	--

This trend (increasing chromium extraction) was also supported by other direct comparisons (Experiment 32 vs. Experiment 33 and Experiment 19 vs. Experiments 28 and 30). Relative to copper and nickel extractions, conditioning of the sludge is of no value.

Leachant Effects

Among early investigations, the effects of the strength of ammonium carbonate-ammonium hydroxide (AMC-AMH) were explored in leaches done at room temperature. Strengths can be categorized as weak (with a 6:5 weight percent ratio of contained NH_3:CO_2 value), moderate (11:9), and strong (25:14). The effects of leachant strength upon extraction were

	Weak	Moderate	Strong
Experiment numbers	1,2,3,15	8,9,11	17
Copper			
Average, percent	52	56	59
Standard deviation	0.7	7.2	--

[a] Details of experimental conditions are given in Appendix A.

	Weak	Moderate	Strong
Nickel			
Average, percent	18	29	23
Standard deviation	5.5	3.2	--
Chromium			
Average, percent	2	6	7
Standard deviation	1.7	3.2	--

These data suggest a slight inferiority in copper and nickel recoveries associated with the use of the weak leachant.

Leaches conducted with only ammonium hydroxide (AMH) (Experiments 12 and 13) resulted in the extraction of the following percentages of metals:

	Average, percent	Standard Deviation
Cu	34	6.4
Ni	6	2.1
Cr	2	1.4

AMH is clearly less effective than AMC-AMH, regardless of strength. Room temperature leaches with only ammonium carbonate were conducted using a strong (supersaturated) mixture. Results for Experiments 16, 18, and 29 were

	Average, percent	Standard Deviation
Cu	57	1.5
Ni	31	13.7
Cr	14	2.1

These results for copper and nickel are comparable to those for "moderate" or "strong" AMC-AMH solutions. The nickel extractions varied from 19 to 46 percent; however, note the high standard deviation values. For AMC leaching, the chromium removed from the sludge was undesirably high.

Ammonium sulfate leaches were conducted at room temperature (Experiment 10) and at 50 C (Experiment 37B). In neither case were extractions promising. Statistics are

	Average, percent	Standard Deviation
Cu	31	2.8
Ni	8	0.7
Cr	0.6	0.6

AMC, AMN, and AMC-AMN leaches exhibit a pH of about 10 or higher on these copper-rich sludges. As a consequence, the leaching of nickel may be difficult. AMS leaches proceed at a lower pH, which should be conducive to improved nickel extraction, but such a result was not observed.

Best results in terms of copper and nickel extractions were obtained with moderate or strong AMC-AMN or the strong AMC leachants.

Temperature Effects

Leaches were conducted at room temperature and at moderately elevated temperatures (50-70 C) using strong AMC or AMC-AMN leachants on either dried sludge or slurries. The average percentage of metals extracted were

	Room Temperature	Elevated Temperature (50-70 C)
Experiment numbers	16,17,18,29	19,20,28,30
Copper		
Average, percent	58	82
Standard deviation	1.5	10.1
Nickel		
Average, percent	32	38
Standard deviation	9.9	9.8
Chromium		
Average, percent	11	10
Standard deviation	4.0	7.5

From this comparison, it is apparent that leaching at elevated temperature is beneficial to copper extraction and probably also to nickel extraction. Chromium segregation appears to be lessened at elevated temperatures, but the elevated temperature results for chromium are biased by a proportionately greater number of leaches conducted on slurries, rather than dried sludge. In general, this analysis indicates a strong preference for performing leaches at modestly elevated temperature, e.g., 50 C.

Leaching Time Effects

Several sets of experiments were conducted illustrating the effects of leaching time. One comparison between the second and third experiment (room temperature, dilute AMC-AMN) indicates modest improvement in copper and nickel extractions attributable to longer leaching time. The percentage of metals extracted were

Experiment number	3	2
Leaching time, hours	20	3
Copper extraction, percent	60	54

Nickel extraction, percent	24	14
Chromium extraction, percent	1	Low

In concentrated leachants at room temperature, the following comparisons are possible of the percentages of metals extracted:

Leaching time, hours	3	64
Experiment numbers	16,17,18	32,33
Copper		
Average, percent	58	68
Standard deviation	1.2	2.1
Nickel		
Average, percent	33	38
Standard deviation	11.9	0.7
Chromium		
Average, percent	10	15
Standard deviation	3.5	4.2

For leaches conducted at 50 C, the following comparison is valid:

Experiment number	19	34
Leaching time, hours	3	64
Copper extraction, percent	90	70
Nickel extraction, percent	49	38
Chromium extraction, percent	12	8

From these results, leaching at room temperature for times substantially longer than 3 hours appears to result in a modest increase in extraction of copper and nickel, but at 50 C, the opposite conclusion appears warranted. Analyses of grab samples taken at 16 and 40 hours during the 64-hour leaching experiment conducted at 50 C (Experiment No. 34) indicated that nickel extraction would have been maximized if leaching had been terminated at about 16 hours. For copper, extraction would have been best if leaching were stopped at about 40 hours. The respective extractions would have been 56 and 92 percent. These results are compatible with a postulated progressive loss of NH_3 values by volatilization from the leaching mixture during extended leaching at 50 C.

Overall, it appears that extending the leaching time beyond 3 hours does result in improved extractions of copper and nickel. The improvements, however, are marginal and probably are not sufficient to justify the added costs that would be involved in substantial increases in leaching time beyond the nominal 3-hour value.

Aeration and CO_2 Sparging Effects

Three experiments (Experiments 8, 9, and 11) were conducted with bubbling of air or CO_2 through the stirred mixture while leaching proceeded. The objective was to promote the higher valence states in the contained copper

and nickel values in the sludge, hopefully, for significant improvements in extraction. This leaching variation was ineffective, as indicated below by percent extractions which do not differ from leaches in which no sparging was used.

Copper	
Average, percen	
Standard deviat	
Nickel	
Average, percen	
Standard deviat	3.2
Chromium	
Average, percent	8
Standard deviation	4.6

Nickel extraction was highest (41 percent) in the CO_2-sparging experiment, but chromium solubility was also undesirably high. Aeration or sparging was concluded to be ineffective.

Liquor-Enrichment Study

In early leaching studies, copper extraction was less than expected, despite reports of AMC-AMN leachant being able to support levels of at least 50 g/l of copper in ore leaching, there was doubt concerning whether or not this was true in the leaching of sludge. To test this, an experiment (Experiment 6) was conducted wherein the same leach liquor was used to leach three fresh samples of dried sludge. Each stage of this experiment was designed to maintain the liquid:solids weight ratio at 9:1. Leached solids were filtered and washed after each stage. The filtrates and wash stock were combined for analysis. The combined filtrates (including a total of 1042 g of wash, some of which was retained in the wet filter cakes) weighed 1692 g and comprised a volume of 1.51 liters. Analyses showed concentrations (g/l) of 11.6 Cu, 0.50 Ni, and 1.6 Cr for contents of 17.5 g Cu, 0.76 g Ni, and 2.4 g Cr. Based on the volume of leachant alone (assuming complete washing and subtracting the wash volume not used as leachant), contents of at least 21 g Cu, 0.91 g Ni, and 2.9 g Cr are supported by the leachant. These support levels appreciably exceed actual returns found in leaching experiments. It was concluded that leachant saturation was not limiting recoveries to any significant degree.

Leaching of Oxides and Hydroxides

When a number of leaching experiments failed to produce what could have been considered satisfactory extractions, it became desirable to evaluate leaching reactions of known oxide and hydroxide forms of the metals copper, nickel, and chromium, both individually and in selected combinations. To this end, eight experiments (Experiments 21-27 and 31) were conducted at 50 C using the strong (supersaturated) AMC leachant. Cupric oxide (Experiment No. 21) was observed to leach slowly but did return 49 percent of the copper value in a 3-hour leach. Nickelous oxide (Experiment No. 22) and

chromic oxide (Experiment No. 23) were not leached to any significant degree (< 5 percent recoveries). The corresponding hydroxides of copper (Experiment No. 24) and nickel (Experiment No. 26), when leached individually, were completely complexed in 2 hours or less (100 percent recoveries). Chromic hydroxide was not affected (Experiment No. 25).

For Experiment 27A, the combined copper and nickel contents (125 g) exceeded the amount that could be supported by the initial amount of AMC added. After leaching for 3 hours, virtually all of the copper had been complexed, but very little of the nickel was returned to solution. The mixture was not filtered but was stored for 21 days. Following this, additional water (0.6 l) and AMC (333 g) were added, the mixture was stirred and heated to 50 C, and leaching was continued for 3 more hours. This resulted in a substantial, but still inadequate, increase in nickel extraction (to 46 percent). At this point, the mixture was filtered and the wet filter cake combined with fresh leachant. Based on filter cake analysis, solids after the first leaching contained about 2 percent copper, 8 percent nickel, and 25 percent chromium. The final leach extracted 64 percent of the contained nickel but only 29 percent of the contained copper. (Chromium returns to solution were < 5 percent.)

In Experiment 31, 32.2 g Cu and 6.2 g Ni, as hydroxides, were leached at 50 C in strong AMC. The leachant in the 9:1 solids:liquid mixture was more than adequate to support full extraction of the contained metal values. Extraction of copper was very good (95-100 percent), but nickel remained largely with the solids and extraction was < 6 percent.

In these experiments, and in corroborative qualitative leach tests on 10-gram samples, it was determinod that the leaching of copper proceeds at a pH value of about 10, and leaching of nickel in AMC solutions proceeds best at somewhat lower pH (8 to 9). So long as copper predominates in the mixture, the pH will exceed a value conducive to good nickel recoveries. Conversely (Experiment 27B), when nickel predominates, its extraction is improved, but,at the lower pH level, extraction of copper is inhibited.

These results, in particular, indicated the desirability of multistage leaches.

Staged Leaching Studies

Five staged leaching experiments were performed. Two of these were three-stage leaches conducted at room temperature in medium-strength AMC-AMN leachants (Experiments 5 and 7). For these, the filter cakes from the first and second stages were dried and ground to provide head stock for the second and third stages. Net recoveries for these leaches are summarized below in terms of percentages of available metal which was extracted into the leach liquor:

	Copper
Average, percent	80
Standard deviation	6.4

Nickel
Average, percent 30
Standard deviation 11.3

Chromium
Average, percent 15
Standard deviation 4.2

Extractions of copper and nickel were modestly improved over single leaches for 3 hours at room temperature but on a par with single leaches conducted at 50 C. Chromium extraction followed this increasing trend (undesirably).

Three variants of staged leaches were conducted at 50 C. These were (1) a two-stage leach, 6 hours per stage (Experiment 35); (2) a two-stage leach, 2 hours per stage (Experiment 36); and (3) a two-stage leach, 2 hours per stage, with AMS as the leachant for the second stage (Experiment 37). Strong AMC was the leachant for both stages in Experiment 35 and the first stage of Experiment 37. Medium strength (11:9) AMC-AMt was the leachant for Experiment 36. In these experiments, filter cakes from the first stage were not dried but were directly returned to water baths for the second stage of leaching. The results of these experiments are summarized as follows in terms of the percentages of available metal extracted from the solids into the leach liquor:

Experiment Number	Type	Cu	Ni	Cr
35	6-hr	92	64	34
36	2-hr	90	53	26
37	2-hr, AMC/AMS	84	56	16

Summary Statistics

Copper
Average, percent 87
Standard deviation 4.2

Nickel
Average, percent 58
Standard deviation 5.7

Chromium
Average, percent 25
Standard deviation 9.0

In summary, the second-stage AMS leach of Experiment 37 was ineffective, as indicated in earlier discussion of leachant type. There appeared to be a slight advantage of extended time (Experiment 35 vs. Experiment 36), neglecting the possible effect of leachants on copper and nickel extractions, but the desired chromium segregation was also degraded by the increased leaching time (or higher CO_2 content in the leachant). Overall, two-stage leaching

resulted in satisfactory copper extractions. Nickel extractions, although improved, were less than satisfactory, according to the criterion set for this study.

Discussion of Leaching Studies

In summary, the preferred leaching conditions defined in these studies are as follows:

Sludge pretreatment--none
Leachant--ammonium carbonate or ammonium carbonate-ammonium hydroxide
Leachant strength--about 10 weight percent contained NH_3
Leaching temperature--about 50 C
Leaching procedure--two stages of leaching, with mechanical agitation. Each stage should be conducted for 2 to 3 hours. Supernatant liquid from the first stage should be removed prior to conducting the second stage.

Based on evaluation of the results obtained in this study, this processing of the Ametek sludge would be expected to return at least 90 percent of the copper, about 60 percent of the nickel, and less than 10 percent of the chromium to the leaching liquids. Solid residues, after leaching, would contain about 0.5 percent each of copper and nickel and about 12 percent chromium. These values may be compared to the initial raw sludge, containing approximately 6 percent copper, 1 percent nickel, and 13 percent chromium.

Reasons for not being able to extract all of the copper and nickel from the Ametek sludge are not known. However, based on the observations of the degrees and time-dependence of extractions of copper and nickel, it is speculated that these metal values may be contained partly as hydroxides and partly as oxides in the Ametek sludge. Crudely estimated, copper is suggested to exist as about 70 percent hydroxide and 30 percent oxide and nickel on the order of 50:50. If this is reasonably accurate, then some fraction of the contained metal values would be refractory regarding ammoniacal leaching, and limits would exist to the complete extraction of metal values from this sludge by this method. The low degrees of extraction may also have been dependent on some unquantified effects of the drying and grinding of most of the sludge used for leaching experiments. Drying the sludge at 110 C may have altered the constitution of the original precipitates produced during waste-water treatment, possibly toward a more refractory form. The effects of lagoon storage prior to sampling also may be speculated as affecting the form in which the metals are present.

The Ametek sludge was the only material upon which studies were conducted. Other copper- and nickel-rich sludges may respond differently to AMC or AMC-AMH leaching. However, it seems likely that, in the treatment of any sludge, some limits to the recovery of metal values by ammoniacal leaching are to be expected. A question of controlling importance would be: Is the extent of extraction that is practical sufficient to reduce the amounts of residual metals to innocuous levels so as to permit virtually unmonitored

and much less expensive sludge disposal? This question is addressed in greater detail in Section 7 of this report.

It had been expected that the chromium extraction by an ammoniacal leaching solution would be negligible, thus allowing virtually complete segregation of chromium to the residual solids. This situation would simplify operations for recovery of copper and nickel from the pregnant liquor, as well as the extraction and recovery of chromium in further treatment of the residue. The ideal chromium segregation appeared to be closely approached in experiments on raw sludge. However, experimental leaching of dried and ground sludge, and particularly of the reslurried, ball-milled sludge, produced less favorable results, and appreciable amounts of chromium were extracted by the leaching solution. Chromium is not strongly complexed by the NH_3 liquid, and chromic hydroxide is too weakly hydrolizable to account for the high extractions observed. The most logical explanation of the higher-than-expected extractions of chromium is the likelihood of the presence of chromate or dichromate ions, which are readily soluble. If, in chromium-reduction treatment of waste water to produce the trivalent state, particles of sludge are generated that retain an enclosed nucleus of a chromate compound, this nucleus could be exposed in the process of regrinding the dried sludge, and particularly in the process of ball-milling the reslurried dried sludge. This hypothetical explanation is in harmony with observations, but whether or not it has a basis in fact is unknown. An argument against this theory was the result of water-washing of the dried sludge described in Section 4 of the report, where only 70 ppm of the 12-14 percent chromium contained was water soluble. This reported value for chromium, however, was suspect, as the water-wash filtrate was amber in color, which suggests a much higher chromium content. To check this, the filtrate was reanalyzed and was found to contain about 0.7 percent chromium, suggesting that about 5 or 6 percent of the chromium in the dried sludge was soluble in water.

CHROMIUM OXIDATION STUDY

As described in Section 4 of this report, duplicate 2-gram samples of the dried filter cake from leaching Experiment 2 were roasted with an excess of sodium carbonate, and the fused mass was water leached to dissolve the converted chromates.

Analysis of the starting filter cake indicated that each 2-gram sample of this material would contain 0.44 g of chromium. Duplicate analyses on each of the two tests indicated that the amount of chromium dissolved was 0.34 g, with a standard deviation of only 0.0064 g. Accordingly, the extraction of chromium from the leached sludge was indicated to be 77 ± 2 percent at the 95 percent level of significance.

This was considered to be an adequate demonstration of feasibility, and no further investigation of the influence of processing variables was conducted.

RECOVERY OF METAL VALUES

Electrolysis

Leaching filtrates prepared from simulated sludges containing copper, nickel, and zinc were evaluated. In addition to these metals, some filtrates contained chromium, iron, aluminum, and other trace metal ions as impurities carried over from leaching of prepared simulated sludges. The filtrate-electrolyte contained ammonium carbonate at a level about equivalent to a dilute AMC leaching liquor (1 molar solution).

The significant differences in behavior during electrolysis were observed for the various solutions examined. There was no apparent effect of varying impurity types or levels.

The open-circuit voltages of the solutions were measured and were about + 0.6 V with respect to the calomel electrode. Current-voltage traces indicated three reduction reactions occurring at overpotentials of

(1) + 0.55 to + 0.34 V, the range for copper reduction

(2) + 0.11 to -0.34 V, the range for nickel and zinc reduction

(3) -0.28 to -0.78 V, where hydrogen was evolved at the working electrode.

In the experimental electrodeposition of copper from these solutions, the current densities (indicative of deposition rates) were inversely related to the concentration of copper in solution. Thus, in electrolytes containing, for example, 6 grams per liter of copper, a current density of 20 mA/cm^2 was observed, but at a copper concentration of 0.6 g/l, current density was about 2 mA/cm^2. For electrodeposition of nickel and zinc (which are both deposited in the same potential range), current densities were not dependent upon concentration but remained quite constant at about 2 mA/cm^2 over a concentration range of 0.1 to 0.01 mole per liter (about 6 and 0.6 g/l, respectively). Current densities were diffusion limited, so that, even with stirring, deposition efficiencies would remain somewhat less than 100 percent.

One of the filtrates, prepared from a simulated sludge that, in addition to copper, nickel, and zinc, contained from about 0.1 to 0.6 g/l of tin, lead, calcium, zirconium, magnesium, and titanium, as well as major chromium, iron, and aluminum contaminants, was used for more detailed electrolysis experiments. This solution was electrolyzed at four different potentials, each potential level corresponding to a current plateau on the current-voltage curves. Deposition times ranged from 10 minutes to 2-1/2 hours. The results were as follows:

(1) At + 0.45 volt and 10 mA/cm^2, the cathode was unchanged; metal was not deposited.

(2) At -0.24 volt and 50 mA/cm^2, a dark red deposit adhering to the platinum substrate was obtained, confirming copper deposition. The deposit was completely stripped from the platinum in 1:1 HNO_3.

(3) At -0.50 volt and 60 mA/cm^2, a red, powdery copper deposit was obtained, which could be stripped from the substrate. Nickel and/or zinc may have been codeposited in small amounts (< 1-10 percent).

(4) At -0.56 volt and 4 mA/cm^2, nickel was deposited in a dense, adherent form from the 0.1 M Ni solution. The deposit did not dissolve in cold 1:1 HNO_3.

These results indicate the technical feasibility of electrolytic recovery of metallic copper and nickel from pregnant liquors from ammonium carbonate leaching. Analyses of the deposits and definitive quantitative experiments were not conducted in deference to the more pressing problem of attempting to define satisfactory leaching methods.

Cementation

Samples of filtrate from leaching Experiment 35A were used for preliminary cementation experiments designed to cement copper and nickel from solution with zinc. This filtrate contained 3.7 g/l of copper and 0.37 g/l of nickel. All cementation experiments were conducted at room temperature.

In the first experiment, 1 gram of zinc strip was added to 20 ml of filtrate (contents = 0.074 g Cu, 0.007 g Ni) and allowed to stand for about 3 hours. The zinc strip lost 0.4 gram in this treatment. Solids that accumulated on the bottom of the beaker were copper colored; the residue was filtered, dried, and weighed. Its weight was approximately 0.1 gram, or slightly greater than the combined copper and nickel content of the original sample. The filtrate was almost colorless instead of the deep blue color associated with copper- or nickel-laden pregnant liquors.

In a second experiment, 200 ml of the filtrate was used to completely dissolve 4 grams of zinc strip in 3 hours. The resultant mixture was filtered. Analysis of the rosy-colored filter residue showed that all of the copper originally in solution had been replaced by the zinc. The blue color, typical of copper- or nickel-ammino complexes, was gone from the filtrate, which was light green in color.

A third experiment was similar to the first, except that 1 gram of zinc powder was used for cementation. Rapid reaction was indicated by frothing, and, within a few minutes, the typical copper-nickel blue color had disappeared from the solution.

An attempt to cement with iron was totally unsuccessful. (Iron will not replace copper or nickel in ammino complexes.)

It was the intent of these preliminary studies to confirm the technical feasibility of the recovery of metallic copper from ammoniacal leach liquor by cementation, and this was successfully accomplished. Quantitative data necessary for an assessment of economic viability were not obtained.

Precipitation with Sodium Aluminate

An alternative method of removing the copper, nickel and chromium from the ammonium carbonate leach liquor is to precipitate the metals with sodium aluminate. In a preliminary test, sodium aluminate was added to a sample of leach liquor by stirring in NaOH and aluminum metal powder simultaneously. The initial and final metal contents of the filtered liquor were as follows:

Metals	Metal Concentration, mg/l		
	Initial	Final	Removal Efficiency
Copper	3700	1.1	99.99+
Nickel	350	2.8	99.2
Chromium	1380	2.1	99.8

Several mechanisms for the precipitation are possible. The copper, nickel, and chromium may have come down as aluminates, if such exist, and are insoluble. Alternatively, the carbonate ion present in the ammonium carbonate solution may precipitate $Al(OH)_3$ by the reaction

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow 2Al(OH)_3 + Na_2CO_3 \quad (1).$$

The precipitated aluminum hydroxide should be an excellent adsorbent for metal ion species in solution. This supposition--and the suggestion that carbonate ion plays an important role in this chemistry--is supported by the fact that no precipitation occurs from metal-bearing leach liquors which contain only ammonium hydroxide (but no carbonate ion) and which are treated with sodium aluminate solution. The addition of solid ammonium carbonate to the ammonium hydroxide leach liquor which contains sodium aluminate causes an immediate precipitation reaction, with removal of the characteristic blue color from the liquor.

LEACHING OF METALS AFTER TREATMENT OF SLUDGE TO REMOVE COPPER AND NICKEL

Residues from the two-stage, ammonium-carbonate leaching Experiments 35A and 35B, and for dried sludge, were analyzed as follows:

	Residue 35B	Residue 36B	Dried, Unleached Sludge
Copper, percent	1.6	1.3	5.9
Nickel, percent	0.59	0.70	1.3
Chromium, percent	13.2	13.0	12.3

Five grams each of the dried residues from Experiments 35B and 36B were stirred with 200 ml of each of two acid media.

(1) Sulfuric acid at pH 4, which simulates an action somewhat more severe than by exposure of the treated residue to very heavy rainfall in the northeastern United States.

(2) One percent by volume glacial acetic acid, which represents an attempt to simulate worst-case conditions in a nonsegregated landfill which is producing a variety of organic acids.

Five-gram samples of untreated dried sludge also were exposed to each acid under identical conditions. Analyses of the resulting solutions after removal of solids are as follows:

Solid Used	Metal	Metal Concentration, mg/l in Sulfuric Acid, pH 4	Metal Concentration, mg/l in Acetic Acid, 1 percent by volume
Residue 35B	Copper	0.08	14.9
	Nickel	< 0.05	5.0
	Chromium	5.4	6.6
Residue 36B	Copper	0.05	10.0
	Nickel	< 0.05	4.8
	Chromium	3.2	6.9
Dried sludge	Copper	0.20	463.0
	Nickel	0.45	51.0
	Chromium	2.4	106.0

As expected, the exposure to organic acetic acid, which is a ligand-former, shows high levels of metals leaching from dried sludge. What was not expected was the remarkable diminution of metals leachability after carbonate leaching for all three metals.

Ammonium-carbonate treatment of dried sludge, as in Experiments 35 and 36, reduced the susceptibility to acid rainwater leaching of copper and nickel from two to four times, as reflected by this preliminary experimental exposure. The opposite is true in terms of the leachability of the chromium upon exposure to simulated acid rainwater; chromium leachability increased approximately 50 to 100 percent. It should be noted that no attempt was made to remove chromium from dried sludge by leaching in ammonium carbonate; rather, the removal of chromium from the original sludge would be the subject of further experimental treatments. It is expected that reduction of the chromium content of dried sludge would produce rainwater-resistant residue, as in the case of copper and nickel.

SECTION 7

PRACTICAL PERSPECTIVES AND ECONOMICS

Studies performed on this program have defined, at least to a first order, the levels of sludge detoxification with regard to copper, nickel, and chromium that can be expected via ammoniacal leaching and soda ash roasting. An order-of-magnitude reduction of these metals in sludge is achievable. They also have indicated that the recovery of metal values (or chemical value in the case of chromium) is technically feasible.

At present, deposits of such sludges of varying quality exist in storage sites at many of the larger industrial metal-finishing organizations. Smaller operations often dispose of sludge by contract haulage to landfills, where allowed by state regulations. Because of near-term environmental regulations and the expectation of more stringent future promulgations, the status of sludge deposits will change. It is certain that existing sludge heaps will not disappear, and, in the near term, they may reasonably be expected to grow.

The potential ecological threat of sludge piles is unknown, but certainly varies on an individual basis, depending on storage-site construction (e.g., whether or not lagoons are lined), stratigraphy and hydrology of the areas where sludge sites are located, and the nature of the sludge deposits themselves. Sludge deposits represent a possibility of future hydrological contamination via leaching and seepage. (Some states, in recognition of this risk, have invoked measures to prevent seepage, such as requiring the lining of storage lagoons with plastic.)

The reduction of metal contents of sludge would have a cost associated with it. Based on the indicated processes (two-stage leaching with electrolytic recovery of copper and nickel, chromium oxidation and recovery as chromic acid anhydride), a flow sheet was derived and costs were estimated on the basis of a plant to process 100 tons per day of raw sludge containing an estimated 20 tons of solids comprising 1.2 tons of copper, 0.22 tons of nickel, and 2.6 tons of chromium. The cost estimate was developed on a "bare bones" basis, and little detail was developed.

The hypothetical plant included the following considerations:

(1) The plant was considered to consist of operations to recover copper, nickel, and chromium.

(2) The process was considered to include

(a) An ammonium-carbonate leach system to extract copper from the sludge with the copper being recovered from this first-stage leach liquor by electrolysis

(b) A second-stage ammonium-carbonate leach to extract nickel from the sludge, with the nickel being recovered from the second-stage leach liquor by electrolysis

(c) A sodium-carbonate roast of the solid residue, followed by a water leach to recover chromium as a solution of sodium chromate, which was further processed to produce anhydrous chromic acid.

(3) It was assumed that 90 percent of the copper was recovered, 60 percent of the nickel was recovered, and 90 percent of the chromium was recovered.

(4) The plant was assumed to operate 24 hours per day.

(5) It was estimated that the capital investment cost for such a plant would be in the range from $3 million to $5 million.

(6) It was estimated that the plant would recover, on a daily basis, 1.08 tons of copper (as metal), 0.13 ton of nickel (as metal), 4.5 tons of chromic acid, and 3.4 tons of by-product sodium sulfate.

(7) It was assumed that the above materials could be marketed at 80 to 100 percent of the currently quoted prices of commercial materials.

The process operations and materials flows, on which the cost estimate was based, are indicated in Figure 1. The copper and nickel recovery circuits reflect the parameters developed during this study, and the chromium recovery sequence reflects the findings of this program and current industrial practice for the production of anhydrous chromic acid (CrO_3). A fuller discussion of the operating conditions and assumptions used to develop the flowsheet and the associated cost are given in Appendix B.

On the basis of the flowsheet, a list of required equipment and sizes was developed and costed. The list of major equipment items is given in Table 6, along with the estimated cost of the various items. In view of the preliminary nature of the cost estimate, the method used to estimate the total capital cost of the plant was to apply a multiplying factor to the "delivered cost of equipment". The cost factor usually used in this method for "chemical-process" or "solids-liquids" types of plants is 3.6.* Because

* Guthrie, K. M., "Process Plant Estimating, Evaluation and Control", Craftsman Book Company of America, Solana Beach, California, 1974; "Cost Engineering" October, 1965 (Industrial Research Service, Inc.; Dover, New Hampshire).

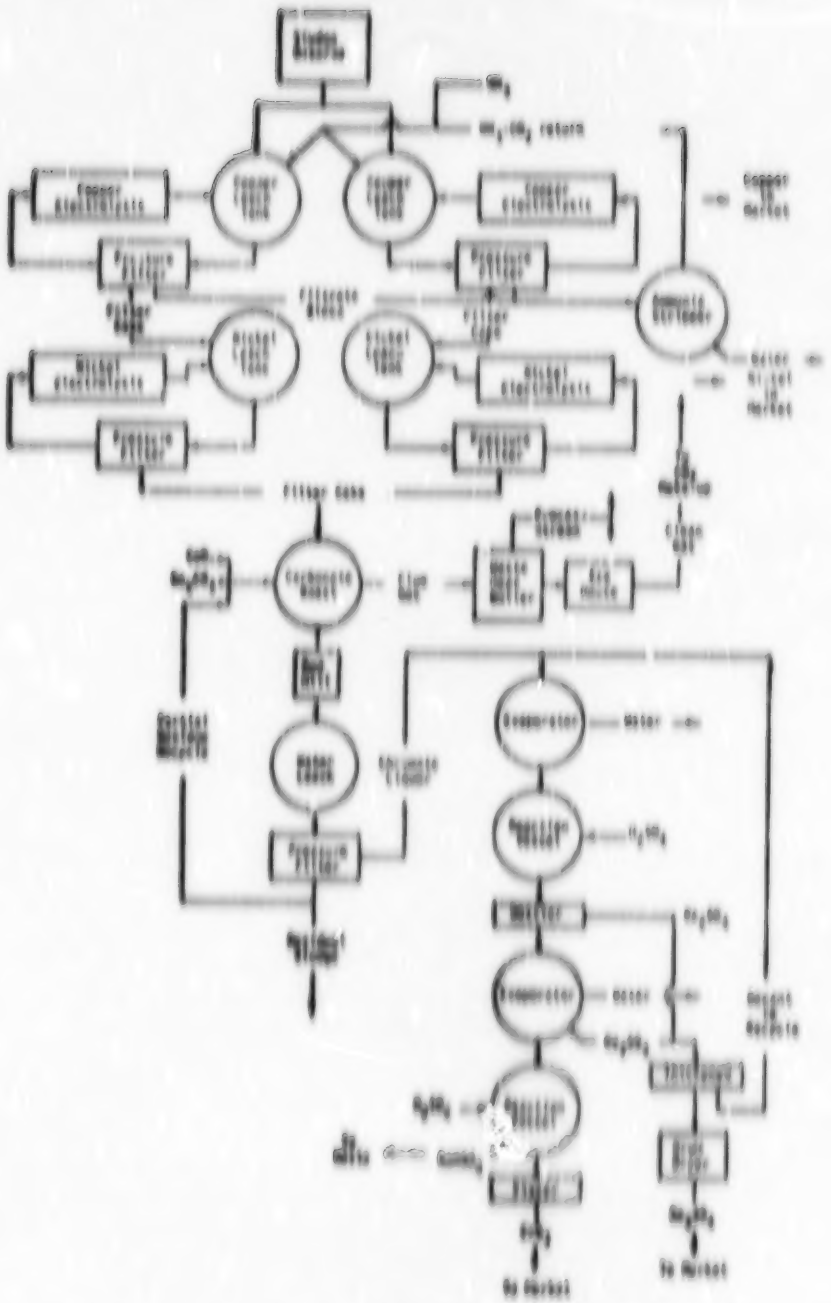

FIGURE 1. FLOWSHEET FOR PLANT COST ESTIMATION

TABLE 6. LIST OF MAJOR EQUIPMENT ITEMS, DELIVERED COSTS, AND TOTAL CAPITAL COST ESTIMATES

Equipment items	Number of items	1975 Delivered Equipment Cost Each $	Delivered Equipment Cost All Items (1975 $)
Copper and nickel leach and electrolysis			
Leach tanks, 4000 gal, steel	4	6,960	27,840
Plate and frame pressure filters, 70 gpm	4	22,050	88,200
Circulating pumps, 70 gpm	8	525	4,200
Bucket elevators, 20 ft high	4	3,375	13,500
Electrolysis tanks, 6200 gal, steel	4	9,930	39,720
Ammonia stripper	1	60,000	60,000
Carbonate roast and chromate leach			
Bucket elevator, 20 ft	1	3,375	3,375
Rotary kiln, 80 tons/day	1	1,020,000	1,020,000
Waste heat boiler and baghouse	-	150,000	150,000
Rod mill, 80 tons/day	1	4,080	4,080
Water leach tank, 4000 gal	1	6,960	6,960
Bucket elevator, 20 ft	1	3,375	3,375
Plate and frame pressure filter, 70 gpm	1	22,050	22,050
Chromate liquor storage tank, 4000 gal	1	6,960	6,960
Chromic acid production			
Evaporator, single stage	1	6,000	6,000
Reaction vessel, 200 gal	1	1,500	1,500
Settler	1	3,000	3,000
Triple effect evaporator	1	7,500	7,500
Thickener (Na_2SO_4)	1	2,250	2,250
Drum dryer	1	1,500	1,500
Reaction vessel	1	1,500	1,500
Flaker	1	3,000	3,000
Total delivered equipment cost, 1975 $			$1,476,510
Total plant capital investment low (factor = 2.0)			$2,953,020
Total plant capital investment high (factor = 3.5)			$5,167,785

of the relatively small size of this plant and the possibility that costs of installation, construction, and support facilities might be minimized in a smaller plant operation, capital investment costs were estimated using factors of 2.0 and 3.5 on the delivered equipment costs. The corresponding estimated capital costs were about $3.0 million and $5.2 million (see Table 6). Correspondingly, two sets of operating costs were developed since some categories of operating costs (e.g., interest depreciation, etc.) depend on capital investment. The two sets of operating costs are shown in Table 7. The daily operating costs are also expressed in terms of dollars per ton of feed and cents per gallon of feed. In both cases of estimated capital investment levels, the costs show an operating loss.

The preceding exercise in costing has certain considerations implicit such as the advantage of scale in the selection of the plant size, the assumption of no cost for the feed material sludge, and the assumption of a 10-year supply of sludge (i.e., about 350,000 tons).

However, the resulting net cost of processing, about $6-17 per ton, may be compared with the existing costs of disposal of sludges to the land.

A survey of charges made by waste-disposal contractors performed in 1973 for the Office of Solid Waste Management Programs of the U.S. EPA reported costs ranging from $6 per ton to $60 per ton.* The range of variation of these costs reflects differences in methods of treatment and disposal, differences in the management of the disposal sites, and differences in overhead and profit margins. It may be further noted that special charges, in addition to those constituting the above range, were made for the disposal of wastes containing hexavalent chromium or cyanide. These costs, supplemented by more current information developed on a subsequent study for OSWMP, produced an average disposal cost (in 1975 dollars, for comparison with the plant operating costs) of $33 per ton, with the same range of costs still persisting.** Thus, it may be considered that the projected plant operating cost of $6-17 per ton may be compared with the alternative cost of sludge disposal ranging from $6 to $60 per ton, averaging $33 per ton.

This cost comparison allows the speculation that, if uniform regulations were promulgated which made the sludge residue from the projected process acceptable, the process might well be the alternative of choice for the treatment of sludges, prior to their disposal to the land.

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* Unpublished survey by Versar, Inc., Springfield, Virginia, for the Office of Solid Waste Management Programs, U.S. EPA, Washington, D.C., September 10, 1974.

** "Assessment of Industrial Hazardous Waste Disposal Practices - Electroplating and Metal Finishing Industry", Final Report on Contract 68-01-2664, to the Hazardous Waste Management Division of the Office of Solid Waste Management Programs, U.S. EPA; September 30, 1976.

TABLE 7. CATEGORIES OF DAILY OPERATING COSTS AND CREDITS

Cost Category	(Low Capital Investment)	(High Capital Investment)
Labor (eight men/shift, $8/hr)	$1,536	$1,536
Chemicals and materials	2,635	2,635
Energy		
Electrical	261	261
Fuel	1,262	1,262
Maintenance (2 percent of capital)	169	295
Insurance (1 percent of capital)	84	148
Taxes (3 percent of capital)	253	443
Interest (8 percent of capital)	675	1,181
Depreciation	844	1,477
	$7,719	$8,705
Credits		
1.08 tons of copper	$1,261	$1,261
0.13 ton of nickel	443	443
4.5 tons of CrO_3	5,220	5,220
3.4 tons of Na_2SO_4	187	187
Total credits	$7,111	$7,111
Net operating costs	-$ 608	-$1,684
	= -$6.00/ton = 3¢/gal	= -$17.00/ton = 8-1/2¢/gal

APPENDIX A. DATA AND ANALYSIS TABULATIONS

TABLE A-1. DESCRIPTION OF LEACHING EXPERIMENTS

Experiment No.	Sample Matrix Description[a]	Leachate Description[b]	Leach Conditions	Mass Leached, g or g/g
1	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]	[illegible]
7	[illegible]	[illegible]	[illegible]	[illegible]
8	[illegible]	[illegible]	[illegible]	[illegible]
9	[illegible]	[illegible]	[illegible]	[illegible]
10	[illegible]	[illegible]	[illegible]	[illegible]
11	[illegible]	[illegible]	[illegible]	[illegible]
12	[illegible]	[illegible]	[illegible]	[illegible]
13	[illegible]	[illegible]	[illegible]	[illegible]
14	[illegible]	[illegible]	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	[illegible]
16	[illegible]	[illegible]	[illegible]	[illegible]
17	[illegible]	[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	[illegible]	[illegible]
19	[illegible]	[illegible]	[illegible]	[illegible]
20	[illegible]	[illegible]	[illegible]	[illegible]
21	[illegible]	[illegible]	[illegible]	[illegible]
22	[illegible]	[illegible]	[illegible]	[illegible]
23	[illegible]	[illegible]	[illegible]	[illegible]
24	[illegible]	[illegible]	[illegible]	[illegible]
25	[illegible]	[illegible]	[illegible]	[illegible]
26	[illegible]	[illegible]	[illegible]	[illegible]
27	[illegible]	[illegible]	[illegible]	[illegible]
28	[illegible]	[illegible]	[illegible]	[illegible]

TABLE A-1. (Continued)

Batch No. (a)	Design basis thermocycle[b]	Leaching test regime[c]	Leach conditions	Data (yes[d] or no)	
19	350 g U-3 C, 5.6 g Ca, 1.3 g Al, 12.1 g Si	MC, [illegible], static, 0.05 S/gW	3 hr, 50 C, pH[illegible]	No	[illegible]
20	Same	"	3 hr, 0.1 , pH[illegible]	No	[illegible]
21	"	"	3 hr, 50 C, pH[illegible]	No	[illegible]
22			3 hr, 50 C, pH[illegible]	No	[illegible]
23	35 g [illegible] + 0 g [illegible], 22.7 g Ca, 6.2 g Al	MC, [illegible], static, 1.0 S/gW	0 hr, 0.1	No	No
24	350 g U-3 , 5.6 g Ca, 1.3 g Al, 12.1 g Si	Same	Same	No	No
25	350 g U-3 , 6.3 g Ca, 1.5 g Al, 14.0 g Si	"	0 hr, 50 C, pH=	No	No
26	350 g U-3 , [illegible]	"	[illegible]	No	No
27	Same	"	Same	No	No
28	350 g wet cake from 25b, estimate 0.0 g Ca, 0.00 g Al, 0.0 g Si				
29	350 g U-3 , 5.6 g Ca, 1.3 g Al, 12.1 g Si	MC, 25, [illegible], [illegible], 0.01 S/gW	3 hr, 50 C	1	Yes
30	350 g wet cake from 29d, estimate 0.00 g Ca, 0.00 g Al, 0.0 g Si	MC, 25, [illegible], [illegible], 0.01 S/gW	Same	1	No
31	350 g U-3 , 6.7 g Ca, 1.6 g Al, 12.9 g Si	MC, Na, [illegible], static, 1.0 S/gW	" C	No	No
32	350 g U-3 , 6.7 g Ca, 0.00 g Al, 12.9 g Si	MC, [illegible], static, 1.0 S/gW	"	No	No
33	350 g wet cake from 25b, estimate 1.3 g Ca, 0.00 g Al, 12.9 g Si	MC, Na, [illegible], static, 1.0 S/gW	3 hr, 50 C	No	No
34	350 g U-3 + 0 g Ca + 1.5 g Al, [illegible] + 12.1 g Ca, 2.5 g Al, 12.9 g Si				

(a) [illegible] batch preparation + subject experiments.

(b) U-3 = the closing test period
U-1 = period 1 [illegible]
U-2-1 = period 1 [illegible], washed with water and rinsed, 0 g weight loss
U = [illegible] (design basis)
Design, cement, and chemical content based on [illegible] analysis, unless otherwise noted; underlined values are based on [illegible] taken from the specific [illegible] for leaching.

(c) MC = [illegible] solution
SW = [illegible] solution
DW = [illegible] solution
Intervals, specified as "Ca, S/gW", the total [illegible] of the total liquid volume, including liquid contained in the [illegible] at each [illegible]. Blank also indicates liquid is [illegible].
[illegible] = a portion of the filtrate was recycled through the filter cake
Ca = [illegible], [illegible]-controlling water
L = Test [illegible] was run in a [illegible].

(d) S/C = [illegible] [illegible], all others are [illegible] filtrate.
Analysis [illegible] [illegible], [illegible] filtrate.
Slurry and [illegible] samples were [illegible] filtered to [illegible] of water [illegible] liquid + [illegible] for 2 hours at room temperature prior to [illegible] to leaching [illegible] and [illegible].

TABLE A-2. [illegible]
LEADING DISPENSERS*

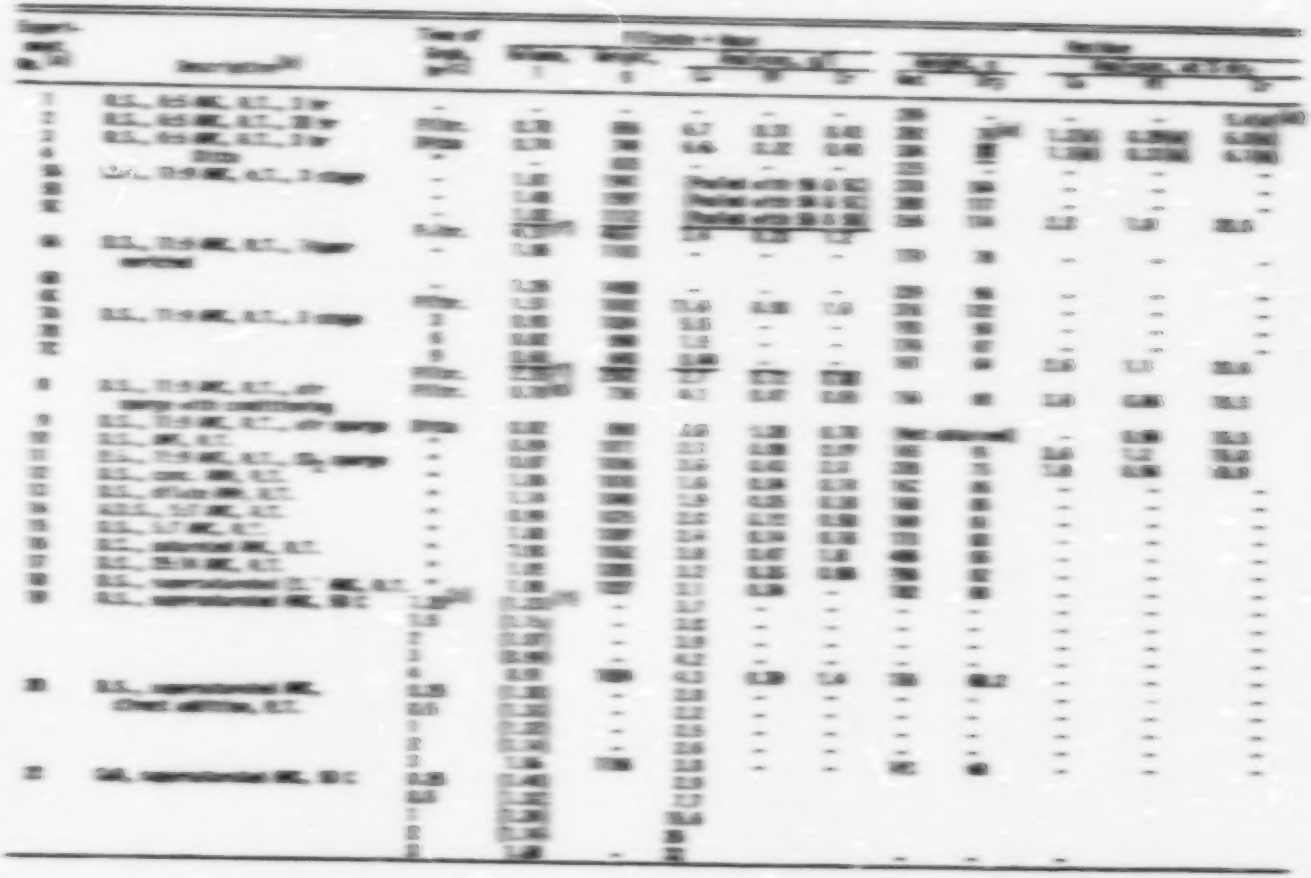


TABLE A-2. (Continued)

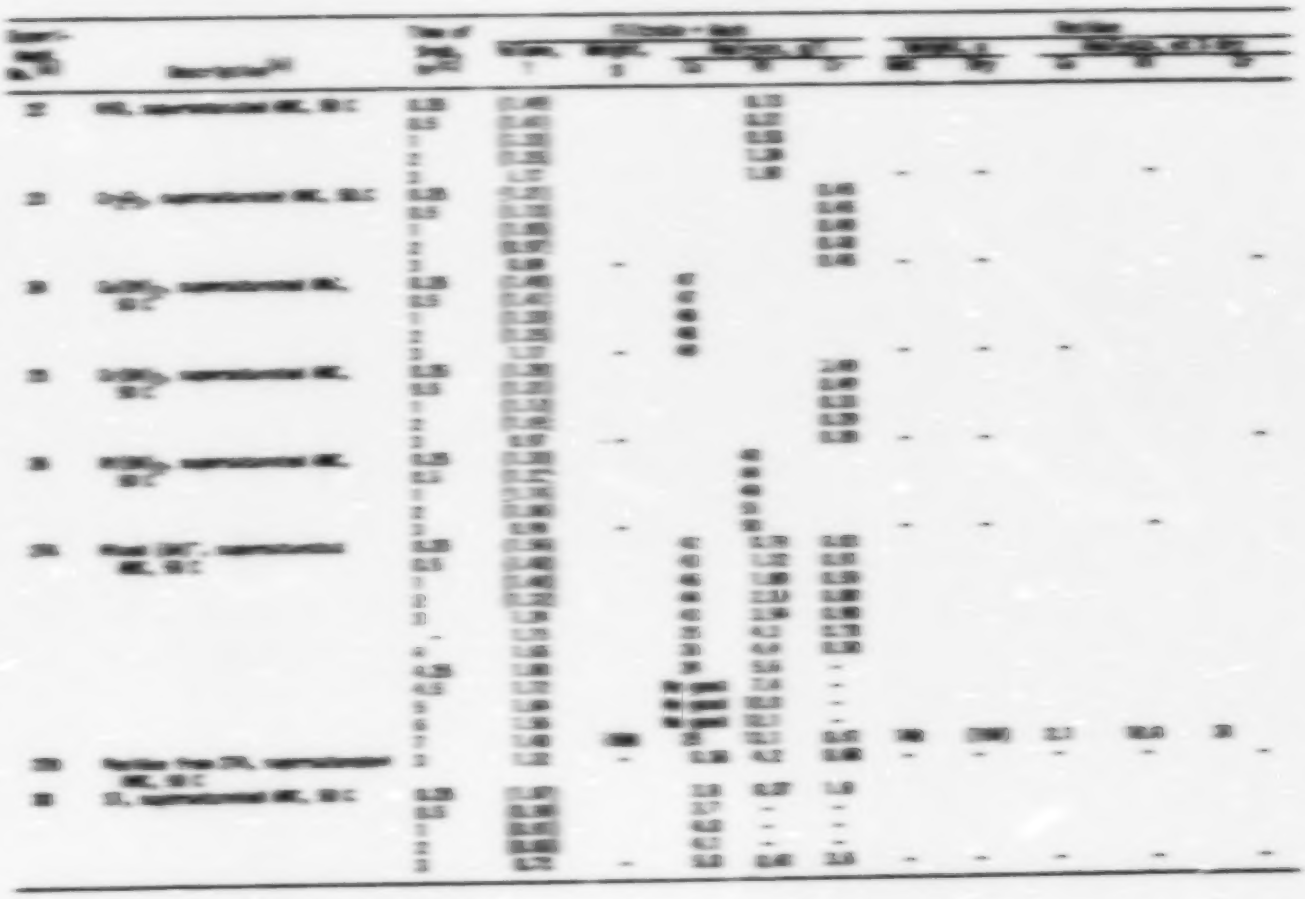
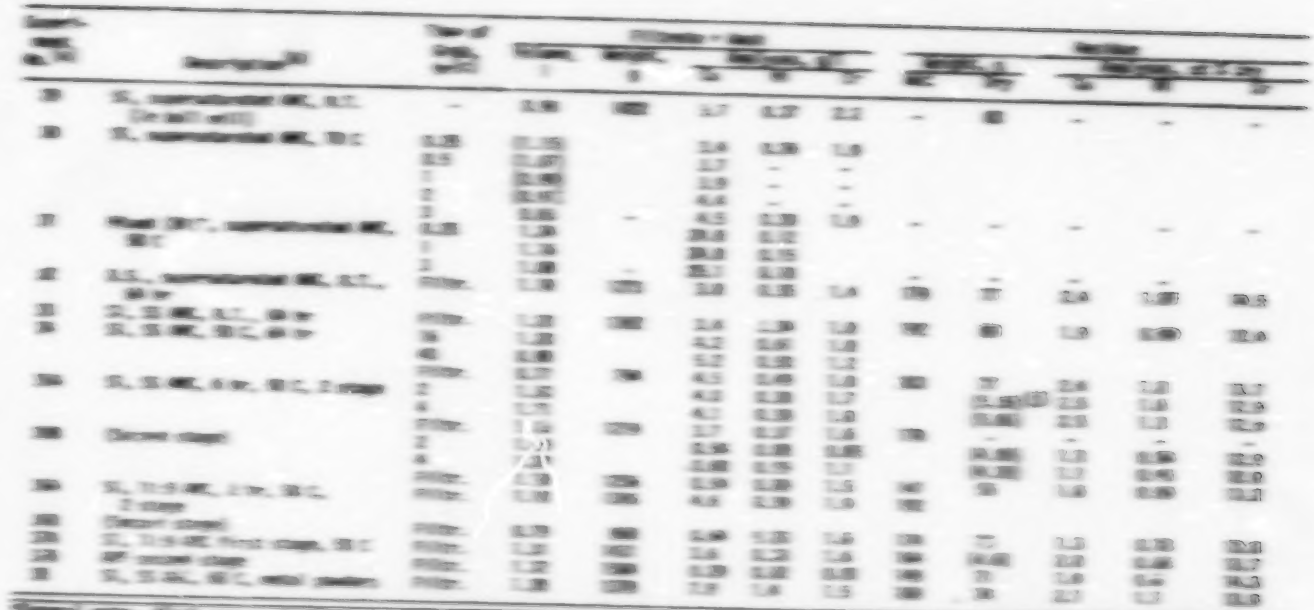


TABLE A-2. [Continued]



[illegible]

TABLE A-3. [illegible]

[illegible]	[illegible]	[illegible]			[illegible]	[illegible]			[illegible]		
1	[illegible]	8.5	1.1	10.9	3	–	–	–	–	–	10.1
2	[illegible]	8.5	1.1	10.9	28	5.2	0.39	0.39	2.6	0.02	10.9
3	[illegible]	8.5	1.1	10.9	7	4.6	0.15	0.39	4.0	0.09	10.5
4	[illegible]	–	–		[illegible]				–	–	–
5	[illegible]	17.4	2.2	30.0	340	14.7	0.09	5.2	2.5	1.34	30.0
6	[illegible]	25.5	4.2	46.3	340	17.5	0.15	2.4			
7	[illegible]	8.7	1.1	77.2	340	6.3	0.39	2.1	1.7	0.78	15.1
8	[illegible]	5.0	0.50	17.0	340	7.9	0.15	0.39	2.5	0.08	12.4
9	[illegible]		[illegible]		–	3.0	0.15	0.39	–	–	–
10	[illegible]		–		3	1.9	0.37	0.37	3.7	1.39	10.6
11	[illegible]		–		3	2.1	0.37	1.7	1.6	0.39	11.9
12	[illegible]		–		3	1.7	0.39	0.15	–	–	–
13	[illegible]		–		3	2.2	0.35	0.39	–	–	–
14	[illegible]		–		3	2.0	0.39	0.39	–	–	–
15	[illegible]		–		3	2.4	0.39	0.35	–	–	–
16	[illegible]		–		3	2.4	0.42	1.5	–	–	–
17	[illegible]		–		3	2.4	0.27	0.39	–	–	–
18	[illegible]		–		1	2.3	0.39	–	–	–	–
19	[illegible]				1.25	4.6					
					1.9	4.7					
					2	4.8					
					3	5.1					
					4	5.2	[illegible]	11.0			
20	[illegible]		–		0.25	2.3					
					0.5	3.0					
					1	3.4					
					2	3.5					
					3	3.9	–	–	–	–	–
21	[illegible]	35.5			0.25	4.1					
					0.5	33.6					
					1	35.2					
					2	36.3					
					3	36.7			–		
22	[illegible]			77.9	0.25		0.39				
					0.5		0.33				
					1		0.33				
					2		1.42				
					3		2.48			–	

TABLE A-2. [illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE A-2. [Continued]

Experiment No.	Description[a]	Grain, Head Size			Layer Thk.	Conductive Zone by Deposition			Conductive Zone by Discharge		
		(a)	(b)	(c)	(in.)	(a)	(b)	(c)	(a)	(b)	(c)
31	Wood [SW], [S-WL], SI-C	32.2	9.9		0.25	30.0	0.15				
					1	30.0	0.18				
					2	31.1	0.22		–	–	
32	S.C., [S-WL], A.T., Sag-clay	7.9	1.7	32.6	0	4.5	0.41	1.7	1.8	0.33	11.2
33	SI, [S-WL], A.T., Sag-clay	6.5	1.5	31.0	0	4.1	0.41	2.2	1.5	0.79	9.9
34	SI, [S-WL], SI-C, Sag-clay	5.9	1.3	32.3	0	5.7	0.73	2.2			
					0	5.4	0.59	1.3			
					0	4.2	0.47	1.0	1.0	0.27	[31.5]
35	SI, [S-WL], S-Fr, S-ridge, SI-C	5.9	1.3	32.3	2	5.2	0.49	2.1	2.1	1.3	16.7
					1	5.3	0.50	2.3	1.9	1.0	9.9
					0	4.0	0.46	2.1			
36	Secret ridge				2	0.70	0.10	1.1	1.0	0.42	16.3
					4	0.70	0.11	1.0	0.42	0.34	9.6
					0	0.72	0.12	1.9	0.40	0.32	7.3
37	SI, [1-S-WL], S-ridge, SI-C	5.9	1.3	32.3	2	5.1	0.48	2.1			
38	Secret ridge				2	0.55	0.10	1.3	0.95	0.33	9.5
39	SI, [1-S-WL], First ridge, SI-C	6.1	0.80	12.9	2	4.7	0.50	2.1	1.6	0.55	11.3
40	[W] second ridge, SI-C	11.3	0.45	10.03	2	0.30	0.03	0.03	1.0	0.43	16.2
41	SI, S-WL, with sand gaskin, SI-C	32.1	2.5	12.0	2	10.0	1.0	1.0	1.0	0.0	16.3

[a] Special features: [same as Table A-1].

(a) S.C. = ice clay
[W] = [illegible], with an offset hydraulic fracture. Strengths given as 0.5 are for [illegible] set wire
S.C. = wood clay
ST = sandstone dry clay
[W] = [illegible]
[W] = [illegible]
A.S.C. = water-backed wood clay.

(b) [ ] Bounding fracture contact on elevated surfaces used as final surface. Any exceptions assuming prior grab sample losses.

(c) [ ] Assuming surface ceramic failure surfaces for softly caused by prior grab sample.

COMMENTS ON CALCULATION METHODS FOR TABLE A-3

1. Cumulative grams to filtrate $= C_i \times V_i + \sum_{n=1}^{i-1} 0.08\, C_n$

   where C_i = concentration, g/l at time i
   V_i = volume, in l., at time i

   $\sum_{n=1}^{i-1} 0.08\, C_n$ = summation of dissolved metal removed in prior grab samples.

   In the case of two or 3 stage leaches, contents of pregnant liquors were added together for calculations, except for experiment 278, which was independently calculated.

2. In leaches of sludge where more than 3 grab samples were removed, recovery calculations were based on head stock contents less the estimated (pro-rata) progressive removal of solid values removed with grab samples.

3. Accountability calculations also consider losses of solids values removed in grab samples, along with estimated or analyzed filtering losses of solids (incomplete recovery of filter cake) for multistage leaches.

[illegible] TABLE A-4. CALCULATED [illegible] ("RETURNS TO SOLUTION") AND ACCOUNTABILITIES FOR LEACHING EXPERIMENTS[a]

Experiment No.	Description[b]	Calculated Recoveries, Percent						Assay			Accountability, Percent		
		Cu	Fe	S	Cu	Fe	S	Cu	Fe	S	Cu	Fe	S
1	[illegible]	–	–	–	–	–	–	–	–	–	–	–	–
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]												
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]										
7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
12	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
13	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
14	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
15	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
16	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
17	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
18	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–	–
19	[illegible]												
20	[illegible]	[illegible]	[illegible]	–	–	–	–	–	–	–	–	–	–
21	[illegible]	–	–	–	–	–	–	–	–	–	–	–	–
				–									
22	[illegible]			–			–			–			
		[illegible]											
		[illegible]											
		[illegible]											
		[illegible]											
		[illegible]			–			–			–		

[illegible]

TABLE B-6. [Continued]

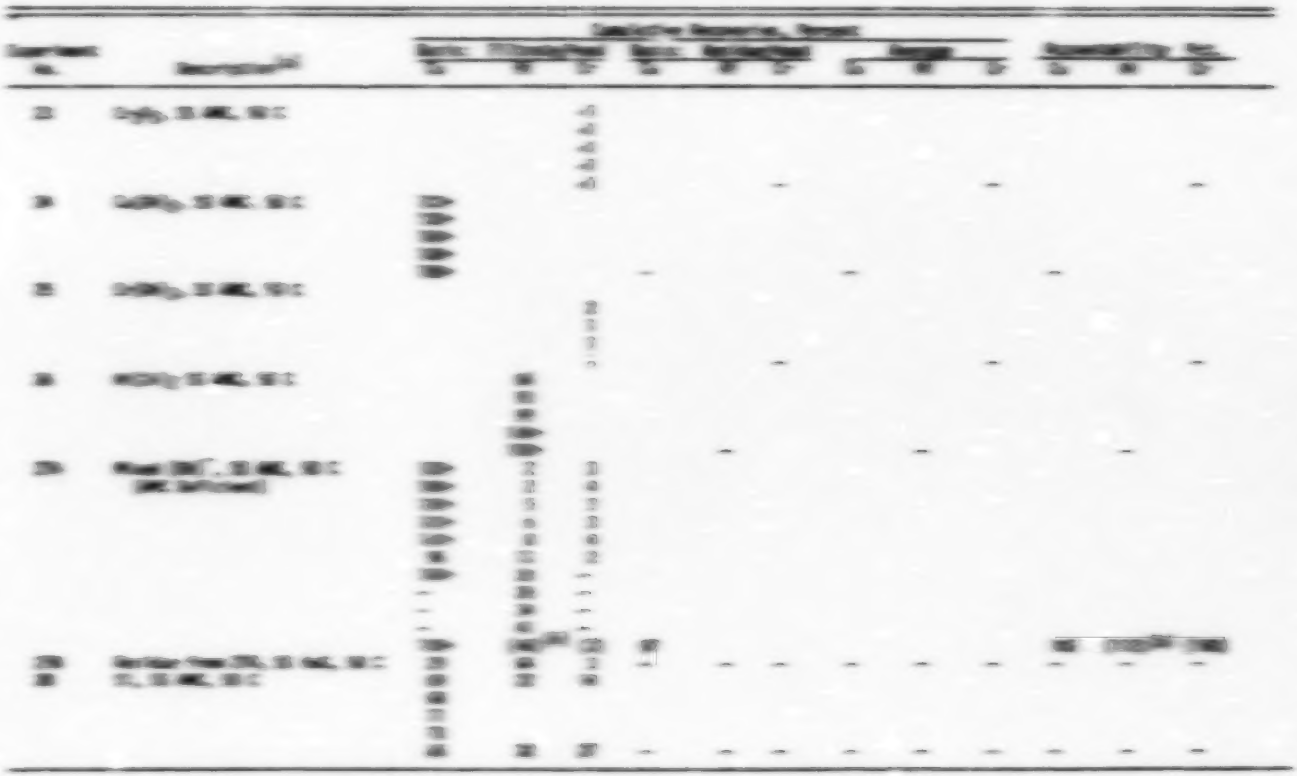


TABLE A-8. [Continued]

Specimen No.	Description[a]	Specific Heat, Btu/(lb)(°F)									

APPENDIX B

ESTIMATION OF PLANT COSTS

The following paragraphs give the major considerations and assumptions on which the plant flowsheet and costs were developed.

The overall considerations for flowsheet development were that the input to the plant would be 100 tons per day of sludge, containing 20 percent solids. The output of the plant was assumed to be copper and nickel metals and chromium in the form of anhydrous chromic acid, CrO_3. The solids were assumed to have a composition similar to the sludge used in this study, namely 6 percent copper, 1.1 percent nickel, and 13 percent chromium (weight percents on a dry basis).

COPPER AND NICKEL LEACHING

Leaching conditions were assumed on the basis of the experimental findings of this study. Each leach was assumed to take 3 hours, using a leach solution containing 9 weight percent ammonia (NH_3) and 12 weight percent CO_2 and a liquid-to-solid ratio of 9 to 1. Leaching was assumed to be done on a batch basis, and two leach circuits were assumed to operate in series, each accommodating five 3-hour leach cycles in 24 hours. The leach tanks were sized to a 4000-gallon capacity and are constructed of mild steel, with covers. Agitation and heat were considered to be supplied by process steam.

PRESSURE FILTRATION

It was assumed that the copper leach liquor would be filtered in pressure filters throughout the leaching cycle, with the cake recirculated to the leach tank, and the filtrate to the electrolysis tanks. Recirculation was assumed to occur three times per leach cycle, or at a rate of about 70 gallons per minute. The pressure filter was assumed to operate at a rate of 30 gallons per hour per square foot and produce filter cake containing 50 percent solids.

COPPER ELECTROLYSIS

The copper electrolysis was assumed to operate at a current density of 15 amperes per square foot, at a current efficiency of 50 percent. It was

estimated that 190 cathodes would be required, each 3-1/2 x 4 feet in a tank containing approximately 6,000 gallons of solution.

NICKEL ELECTROLYSIS

The nickel leach, filter, and electrolysis circuits were considered to be the same as for the copper circuit.

AMMONIA STRIPPER

Because of the introduction of 80 tons of water per day into the leach circuit with the raw sludge, it was assumed that a leach liquor bleed stream would be steam-stripped to produce an NH_3-CO_2 concentrate for recycle and reconstitution of the solution added to the copper (and nickel) leach tanks. The stripping operation was assumed to be 97 percent effective.

LEACH REAGENT LOSSES AND MAKE-UP

The stripped leach solution represents losses of ammonia and CO_2 in solution since the stripper is assumed to operate at less than 100 percent efficiency. The other loss of reagents was assumed to occur in the filter cake from the nickel circuit, which was considered to be 50 percent by weight solids with the balance being leach solution. It was estimated that 2.2 tons per day of make-up ammonia would be required and would be supplied in the form of purchased anhydrous ammonia. Also, it was estimated that 2.9 tons/day of CO_2 would be required to be replaced and would be obtained from cleaned flue gas from the carbonate roasting furnace.

CARBONATE ROAST FURNACE

Based on industrial process descriptions, it was assumed that the charge to the carbonate roasting furnace (which was assumed to be a rotary furnace) would contain 40 short tons of filter cake per day, along with 10 tons per day of lime (CaO), 12.5 tons per day of sodium carbonate (Na_2CO_3), and recycled residue to total 80 tons per day input. The rotary furnace was assumed to be equipped with a waste-heat boiler and a baghouse to control pollution, produce process steam, and permit reclamation of CO_2 for use in the leach circuit (as needed).

CHROMATE LEACHING

Chromate leaching was assumed to be done at a liquid-to-solids ratio of 5 to 1 and to produce a liquor which was 20 percent by weight sodium chromate. The filtration of the chromate liquor was assumed to produce a filter cake of 50 percent solids which represents the residue of the process.

CONVERSION OF CHROMATE LIQUOR TO CHROMIC ACID

The process was assumed to be that described for current commercial practice. The sodium chromate solution is evaporated to 40 weight percent sodium chromate, reacted with sulfuric acid to produce sodium dichromate and sodium sulfate, evaporated again to precipitate the sodium sulfate, which is assumed to be dried and sold at the rate of 3.4 tons/day. The sodium dichromate, concentrated to 85 percent by weight, is reacted with sulfuric acid and separates into chromic acid anhydride (CrO_3; 4.5 tons per day), which is sold, and sodium bisulfate (5.4 tons per day), which is assumed to be wasted.

The production of chromic acid consumes 6.6 tons per day of sulfuric acid and represents the second major fuel consumption component because of the evaporation of some 30 tons of water per day.

BASIS OF COSTS FOR EQUIPMENT AND REAGENTS

Most of the equipment costs were developed using information from the reference "Process Plant Estimating, Evaluation, and Control", K. M. Guthrie, Craftsmen Book Company of America, Solana Beach, California, 1974. A few equipment costs were developed using recent design data and costs from concurrent studies by co-workers. Reagent costs were taken from the "Chemical Marketing Reporter" of July 5, 1976, and included the following values:

Ammonia	$185/ton
Lime	$30/ton
Sodium carbonate	$60/ton
Sulfuric acid	$50/ton
Chromic acid	$0.58/pound
Sodium sulfate	$55/ton

Prices for copper and nickel were obtained from "American Metal Market" for July 11, 1976, as $0.73/pound for copper and $2.20/pound for nickel. A factor of 1.33 was applied to these prices to estimate the costs of fabricated starting sheets for the electrolysis bath.

All equipment costs were converted to 1975 dollars using cost indexes from "Chemical Engineering", July 5, 1976, page 7. Factors relating "fob" equipment costs to installed costs were taken from Guthrie (cited above). Operating costs were estimated using allowances as being used in currently published cost estimates for maintenance, taxes, insurance, and interest; these and the assumed 10-year, straight-line depreciation rate are indicated in the table of operating costs and its footnotes.